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WATER-ANALYSIS:

A PRACTICAL TREATISE

ON THE

EXAMINATION OF POTABLE WATER.

BY

J. ALFRED WANKLYN

AND

ERNEST THEOPHRON CHAPMAN.

THIRD EDITION,

ENTIRELY REWRITTEN BY

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PREFACE TO THE THIRD EDITION.

SINCE the publication of the second edition of this book, science has sustained a great loss in the premature death of my friend and colleague, Mr Chapman: and in reconstructing the book, I have him no longer to help me.

The ammonia-process which chemists owe to him, no less than to Smith and to me, has created Water-Analysis for sanitary uses; and has at length won its way to almost universal adoption. In the year 1867 it was employed by Mr Way in his investigations for the Royal Commission on the Pollution of Rivers. In the same year it was used by its inventors for another Royal Commission which inquired into the Water-supply of Towns. Since that period Dr Angus Smith has made a most laborious investigation into the state of the atmosphere in towns and other places, and in the course of this investigation has made most abundant use of the ammonia-process. The Governments of India and of the United States have likewise adopted the ammonia-process in their official investigations.

In the Appendix to former editions of this book we reprinted our reply to certain misstatements made by Dr Frankland to the Chemical Society. Inasmuch as chemists in general have followed the advice we gave them, and have abstained from the employment of Dr Frankland's process, we do not consider that there is any longer any necessity to reproduce our criticism on the Frankland and Armstrong process.

117 Charlotte Street, Fitzroy Square, London,
22*d April* 1874.

PREFACE TO THE SECOND EDITION.

THE present edition of this work differs from the first in containing some new matter. The whole of the last edition has been transferred, almost without alteration, to the present one, though the arrangement has been slightly altered. The new matter added consists of the following :—

The Titration of Waters, added to the chapter on Hardness ;

A Modification of the Process for the Estimation of Nitrates ;

A chapter on Volatile Organic Matter present in Water ;

A Method of Estimating Minute Traces of Lead ; and

A chapter on the Purification of Water.

The present Editor alone is responsible for the form in which the above additions appear, though to Professor Wanklyn must be ascribed the origin of some of the processes here worked out in detail. This remark refers more especially to the estimation of lead. The chapter on the Purification of Water is entirely the addition of the Editor.

The process for the estimation of nitrogenous organic matter in water has, since the publication of the first edition of this work, been employed by Dr Arthur Ransome, M.A., for the examination and estimation of the organic matter of human breath in health and disease. It has also been employed by the Editor for the estimation of nitrogenous organic matter contained in air.

April 1870.

PREFACE TO THE FIRST EDITION.

THIS book is designed to give an account of that kind of Water-Analysis which is proper for the examination of water intended for domestic use. In giving processes of analysis, we have been careful to prescribe only such operations as are practicable. Especially we have kept in view the necessity of economy in time. The complete examination of a sample of water, as set forth in the following pages—viz., the determination of solid residue, hardness, chlorine, nitrogen as nitrates and nitrites, ammonia, and organic matter—may be all done in the space of six hours, whilst a partial examination takes a very short time. In thus economising time, we do not think that we have made any sacrifice for accuracy.

The process for determining nitrogenous organic matter, termed by us the *ammonia-method*, and proposed by Mr Miles H. Smith, and ourselves, at a meeting of the Chemical Society last year, occupies a prominent place in this work. A section of Chapter V.* is devoted to a discussion of the interpretation to be given to the data furnished by that process. The process by Frankland and Armstrong is not given in the text. We believe that the great length of time and great skill requisite to execute it, would render it quite impracticable, even if it were otherwise desirable. Moreover, we do not set any value on its indications. Our objections to it are given in the Appendix.

A prominent feature of this work is its copiousness in examples, more especially in examples of the new determination of nitrogenous matter. In fact, in this time of Governmental water-commissions of different kinds, we have issued a kind of private water-commission of our own, and availing ourselves of the resources of the Ammonia-Method, report on the state of the London, Manchester, Edinburgh, and Glasgow water supply during last summer.

We believe that this is the first book which has been published on Water-Analysis. Up to the present time, the subject has been treated of in a special section in works devoted to *chemical analysis in general:* as, for instance, in the admirable analytical treatise by Fresenius, and in Dr Noad's excellent Manual, from which we quote *verbatim* an account of Clark's method of determining the hardness of water. The subject has also been handled in the "Handwörterbuch," and in Watts' "Dictionary of Chemistry," wherein will be

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* *Vide* appendix to present edition.

found a very admirable article on Water, written by Dr Paul. "Discourses" on the Analysis of Potable Water have also been given to the Chemical Society by Dr W. A. Miller, and by Dr Frankland and Mr Armstrong, and are to be found in the Journal of that Society.

We have freely availed ourselves of all material within our reach. In particular, to Dr Miller's "Discourse," just referred to, we are indebted for an account of the preparation of the Nessler-test. This test, which we believe to be the most delicate known to chemists, was first rendered quantitative by the late Mr Hadow and Dr Miller. The account of the test, which appeared in the "Laboratory" last year, was taken from Dr Miller's "Discourse." The account given in this work is essentially Dr Miller's, being slightly modified, however, in accordance with the dictates of our own rather large experience in the practical working of the test.

To Dr Frankland we are indebted for the account of the determination of nitric acid by the modification of Walter Crum's method. This we have quoted from the *Journal of the Chemical Society,* giving it in addition to the determination of nitric acid by the modification of Schultze's aluminum-process, which we prefer to recommend. We agree with Dr Frankland in the light estimation in which he holds the "loss on ignition." We go with him, also, a long way in his condemnation of the "permanganate test," as a trustworthy measure of the organic impurity of water. In other respects relating to Water-Analysis, we are for the most part at variance with him.

On the subject of the invalidity of the determination of organic matter in water by Frankland and Armstrong's combustion process, we believe that chemists in general agree with us.

A considerable part of this book is new in every sense of the word. The treatment to which we have subjected Clark's table is novel. The fact of the extreme constancy (organically considered) of the good water supply all over the country is here announced for the first time. The great advantage of filtration, and of the application of Clark's softening process to the purification of water, is brought out in this work. The fact that the carbonate of lime carries down albumen in preference to such substances as urea is new. The estimations of nitric acid and ammonia without distillation are new. Other things that are new will be found by our readers.

Laboratory of the London Institution,
May 1868.

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WATER-ANALYSIS.

INTRODUCTION.

Medical authorities are, at the present time, pretty well agreed that if the water of a well, which has received the excreta of a patient suffering from cholera, or from typhoid fever, be drunk, there is the utmost danger that the drinker may contract these diseases. It is also a received fact that the drinking of water, which contains an undue proportion of organic filth—even assuming specific poison to be absent—is injurious to health. Such being the case, the first questions which the sanitarian asks, respecting a given specimen of water which is proposed for use as "potable water," are—Does it contain these septic poisons? Is it abnormally charged with organic filth?

To both these questions the water-analyst is enabled, by the ammonia-process, to answer, in many instances, by an absolute No. In other cases he can show that the water is abnormally filthy; and, in some cases, that there is danger of specific poison.

In the proper place (Chapter IV.), the ammonia-process will be minutely described and explained. Here, however, some of the general results which have flowed from the diligent employment of this process during the last seven years may be briefly summarised.

First, it may be mentioned that the ammonia-process is easily able to detect one part of albumen, gelatine, organic alkali, &c., mixed with ten million times its weight of water. Armed with an instrument of this power, my colleagues and myself have proceeded to investigate the condition of natural waters, and have arrived at the following general conclusions :—

There are deep spring waters—*i.e.*, the water from the Greensand and the Caterham water, which do not contain even this small proportion of nitrogenous organic matter.

So pure (organically considered) are these waters, that it is with difficulty even that the chemist prepares distilled water to vie with them in purity. The water which, after being stored in reservoirs and filtered, is served out by water companies to English and Scotch towns, is likewise, as a rule, in a state of high purity. Not indeed to the supreme degree reached by deep springs, does the town water-supply attain; but still, whatever the source whence it draws its supply, the town-reservoir discharges surprisingly pure water, if only an honest filtration be performed by the water company.

Leaving the pure, deep spring water, and the fairly pure water of the town water-works, we have found unfiltered river water to be, as might be expected, of variable quality. Sometimes this, too, is fairly pure; but at other times, as when the River Thames has received the Fleet-ditch sewer, it is abominably filthy. The surface well is most capricious in quality. It may be fairly pure, or it may be disgustingly foul. Of all the kinds of water that are drunk, the dirty water from the surface well is the most dangerous. Cholera and typhoid fever may be imbibed along with it; for whilst the water of the well may be dilute urine, or drainage from excrement, the degree of dilution is not necessarily so great as to deprive the poisonous materials of their power.

By the aid of the ammonia-process we are now able to divide potable waters into two broad classes, (1), waters which are clean (*i.e.*, which are devoid of any excess of nitrogenous organic matter); and (2), waters which are dirty (*i.e.*, charged with an abnormal quantity of organic matter).

If a water belong to the second class, a knowledge of its history, and, of course, of its mineral constituents, may be of assistance in forming a judgment as to the degree of risk attendant on its employment for domestic use.

In addition to being injurious by reason of organic impurity, water may also be injurious on account of its mineral constituents. These latter may be too excessive in amount, as in the notorious instance of sea-water, or they may be poisonous in themselves. An examination of potable water should therefore include a determination of the amount of inorganic solids in the water, as well as a testing for poisonous metals.

For most sanitary purposes a water-analysis is complete when it includes these data—

Total solids,
Chlorine,
" Free and albuminoid ammonia,"
Poisonous metals.

After giving in Chapter I. a few short directions as to the collection of samples of water, we shall devote a chapter to each of these data in succession; and after that we shall, in Chapter VI., discuss the drawing up of reports, and the conclusions which follow from the analyses. In subsequent chapters the further examination of the water-residue will be dealt with, and also the hardness, nitrates, and gases. A chapter will be devoted to the purification of water, and a final supplementary chapter to the analysis of urine and sewage.

CHAPTER I.

COLLECTION OF SAMPLES OF WATER.

The quantity of water which the water-analyst should direct to have sent to him for analysis should not be less than half a gallon; unless, indeed, there are difficulties in the way of getting so much. In case of necessity, however, a very small quantity of water may be made to do, if extreme care be taken that the bottle be perfectly clean.

The most convenient kind of bottle for holding the half-gallon of water is the stoppered glass bottle, known as the "Winchester Quart," the capacity of which is about half a gallon, and which is to be obtained at most druggists' shops in this country.

Great cleanliness should be insisted upon; and by way of ensuring this, the direction may be given to pour into the bottle a little strong sulphuric acid, and allow it to flow over the inner surface of the bottle, and then to pour in water and shake up, and then to wash with water until the rinsings are no longer acid. Before being charged with water, the bottle should be rinsed out with some of the same kind of water as that which is to be analysed. The bottle having been charged with the sample of water, care must be taken that it should be nearly, but not quite full; and that having been attended to, the stopper should be inserted and tied over with a piece of clean linen or calico.

The employment of linseed meal, almond paste, &c., as lutings, is to be most strenuously avoided; but if anything of the sort be required, a little sealing-wax is, perhaps, the least objectionable.

Although it is preferable to have a glass stopper, still a clean, new cork will do, and in the course of our experience we have never known any harm to arise from a clean cork. The sample of water should be kept in a cool and dark place until it is examined; and the examination should, if possible, take place within forty-eight hours after the collection of the sample.

In making examinations of the water-supply to towns, it is well to draw the water direct from the street mains; and the water-jets at the cab-stands in London offer special facilities for the collection of samples of the water supplied by the different water companies. In order to get a fair sample, it is a wise precaution to allow a little water to run away, so as to clear the pipe before collecting the sample.

If the water to be examined be that of a river or pond, the entrance of scum into the bottle should be avoided by immersing the bottle in the water, and taking care that the mouth shall open at a little distance below the surface. In the case of the river, the middle of the stream should be selected, and the outlets of sewers and feeders should be avoided; a note should also be made whether there has been heavy rain or long drought.

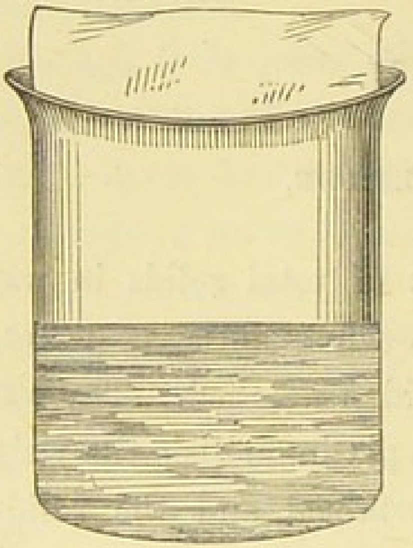
CHAPTER II.

TOTAL SOLID RESIDUE.

THE determination of the amount of total solids in water is a very simple operation. A known quantity of water is evaporated to dryness, and the residue weighed. The water should be evaporated to dryness in a platinum dish, the weight of which has been previously ascertained, and the residue, which, after the water has evaporated away, adheres to the dish, is subsequently weighed along with the dish.

The exact details of the operation are the following :—The platinum dish is cleaned so as to be quite bright. It is then put into hot water, wiped, and allowed to remain for a few minutes in contact with a massive piece of iron (a flat soothing-iron, with the handle knocked off, will answer very well), or else it may be left to cool in contact with a slab of porcelain.

Having been thus got into exactly the same condition as it will be in after the evaporation, it is to be weighed. Then it is to be placed in the water-bath, which consists of a beaker containing boiling water, and of such a size that the platinum dish may rest conveniently in its mouth (*vide* fig.) A small piece of filter paper may be inserted between the dish and the glass, in order to allow vent for the steam. Into the platinum dish 70 cubic centimetres of the sample of water are to be poured ; the water in the bath is then set to boil by help of a lamp, and kept boiling until the water in the platinum dish has evaporated away. In the course of an hour this will have taken place, and the residue in the platinum dish will soon dry. The dish is allowed to remain in the bath for about ten minutes after it appears to be dry (in order to ensure complete dryness), and then removed from the bath, wiped externally, allowed to cool for a few minutes in contact with the iron or porcelain, and weighed. If the weight of the empty dish be subtracted, the weight of the water-residue will be obtained.



In this way we obtain the weight of the solid residue left by 70 c. c. of water. Now, one gallon of water weighs 70,000 grains, and 70 c. c. of water weighs 70,000 milligrammes; so that 70 c. c. of water is a sort of miniature gallon, wherein the milligramme corresponds to the grain. If we know the number of milligrammes of residue which 70 c. c. of water leave, we know the number of grains of solids in a gallon of the water. To make everything clear we give an example :—

Quantity of the sample of water taken, equals 70 c. c.

Weight of dish and residue .	55·500	grammes.
Weight of empty dish . .	55·421	„
	·079	

Therefore the total solids in this sample of water amounted to 79 grains per gallon.

In taking the total solids in water, a number of little modifications of the process, as above described, may be made. Instead of being contented with a simple drying at 100° C. in the water-bath, some chemists prefer a drying at 130° C. in the air-bath. Instead of taking only 70 c. c. of water, a larger quantity may be taken; and this is advisable if the balance or weights at the disposal of the operator be defective.

Very concordant results, and results quite good enough for all practical purposes, may, however, be obtained by operating on small quantities of water. Thus we have obtained

71·89 grains of solids per gallon,
72·10 " " "

in two experiments on the same sample of water, and also

24·64 grains of solids per gallon,
25·13 " " "

It will sometimes happen that the solid residue is very deliquescent; in such a case it must be rapidly weighed.

The evaporation of large quantities of water involves error, from dust getting into the water, and a certain amount of destruction of the organic matter present in the water, and the advantages gained by having a larger water-residue to weigh are counterbalanced by the error arising from the prolongation of the evaporation.

In order to give an idea of the amount of solid residue which actually occurs in natural water, we subjoin a few examples—

	Grains of total solids in a gallon.
London. Thames Companies	18·5
„ New River	17·6
„ Kent Company	26·5
Manchester Water Supply	4·7
Glasgow. Loch Katrine	2·3
Bala Lake	3·2
Guildford. New Supply	19·7
Scarborough Reservoir	28·7
The Rhine at Basel	11·8
Spree at Berlin	8·0
Atlantic Ocean	2688·0
Distilled water	0·1

With the exception of the sea-water, all these waters are, so far as the total solids are concerned, fit to drink; and, on inspecting the above table, it will be seen that the water supplied to the metropolis contains four or five times as much solid matter as the water supplied to Manchester and to Glasgow. The healthiness of London is higher than that of Manchester and Glasgow; and although we should be unreasonable if, overlooking the fact that sanitary conditions are very numerous and very complex, we were to attribute the superior healthiness of the metropolis to the state of its water-supply exclusively, we are, I think, warranted in maintaining that a high solid residue in drinking-water can have no very markedly injurious effect on the public health; and that the experience of London proves it.

In the instance of the London water-supply, the major part of the solid residue consists of carbonate of lime; and, if we subtract the carbonate of lime, the rest of the solid residue will be seen to be not very much higher than that of the water of Manchester and other naturally soft waters.

The excellent new water-supply to Guildford is likewise in the same predicament. According to an analysis made a few years ago, this water contains 14·7 grains of carbonate of lime, and 5 grains of other salts, including some sulphates. Of the nature of the solid residue in the Scarborough water, we have not at hand any very specific information; but most probably the same will be found to hold good in that case.

In the course of his work, after the water-analyst has obtained the solid residue and weighed it, he will do well in making a slight examination of it. If a few drops of hydrochloric acid be poured on it, effervescence will generally occur. This shows the presence of carbonates, which almost invariably consist of carbonate of lime. This qualitative examination for carbonates consumes hardly any time, and should hardly ever be omitted, inasmuch as a knowledge whether or not there are carbonates in the water is useful in various ways.

The water-residue in the platinum dish may likewise be gently ignited, and the observation recorded, whether it blackens during the ignition. The weight of the residue after ignition may likewise be taken. Formerly, before the recent development of water-analysis, the loss on ignition was regarded as a very important datum, and as indicating the quantity of organic matter in the water; but now, we know that the loss on ignition is valueless for any such purpose. The only purpose which a weighing of the ignited residue now serves, is that it affords a check to the determination of total solids. In Chapter VII., an easy method of determining the carbonate of lime in water, and the "solids not carbonate of lime," will be described. We do not give it in this part of the book, because it requires some time for its accomplishment, and because it is not usually required in the ordinary analysis of potable water.

In conclusion, we will remark that if the solid residue do not exceed 30 or 40 grains per gallon, there is, on that account, no reason for rejecting the water for domestic use.

CHAPTER III.

CHLORINE.

Chlorine occurs in drinking-water in combination with sodium and the other alkali metals, and also in combination with calcium or magnesium. The amount of chlorine in drinking-water is, in itself, a matter of very little importance; for, since common salt is an article which we require and take, in some shape or other, every day of our lives, it can be of very little consequence whether or not we take some of it in the water which we drink. The water-analyst resorts to measurements of the chlorine in water, because the presence of chlorine is, in some indirect manner, an indication of sewage contamination.

In order to understand how this comes about, and also to what extent chlorine is indicative of sewage, a little explanation will be necessary. In the first place, natural water which is uncontaminated with sewage is often almost free from chlorine. Urine and sewage, on the other hand, are, comparatively speaking, highly charged with chlorine, which usually exist in them in the form of common salt.

If then a given sample of water be found to be devoid of chlorine, or very nearly devoid of chlorine, it cannot have been charged with sewage. Hence, it occasionally happens that the finding of little or no chlorine in water is a valuable criterion of purity. Here, however, the remark may be made that animal, or sewage, contamination is not the only organic contamination. Vegetable contamination is undoubtedly to be avoided in drinking-water, and against this form of contamination the absence of chlorine is no guarantee. When water is found to contain much chlorine, there is reason for suspecting the presence of sewage; and a further examination of the water is called for.

I am of opinion that too much stress has been laid on the chlorine in drinking-water, inasmuch as it is by no means rare to find an excessive quantity of chlorine in very pure water; and I know that, by reason of the chlorine, pure water has been condemned by water-analysts.

The circumstances in which chlorine-determinations in drinking-water would be of most service, are when time presses, and when the general character of the water of the district being known, it is required to pronounce at once on the condition of a number of wells. Such a case might arise during an outbreak of cholera, when it might be necessary to decide at once on the character of all the wells of a town; and such is the ease with which the chlorine may be measured, that a hundred waters might be examined by one man in the course of a day. At such times I can conceive that the determination of the chlorine in drinking-water might prove of inestimable value.

In order to make a determination of chlorine in drinking-water, we avail ourselves of the well-known reaction of silver-salts on soluble chlorides. When a solution of nitrate of silver is mixed with a solution containing chlorides, the insoluble chloride of silver is produced; and the quantity of chlorine in water may be determined by ascertaining how much of a standard solution of nitrate of silver is required, in order to precipitate all the chlorine in a certain volume of the sample of water.

The standard solution of nitrate of silver is made by dissolving 4·79 grammes of pure nitrate of silver in one litre of distilled water. This solution is then of such a strength, that one cubic centimetre of it is capable of precipitating exactly one milligramme of chlorine.

If some of this standard solution be dropped into a water containing chlorine, a white precipitate of chloride of silver will continue to form, until all the chlorine in the water has been used up; but, as may be readily seen on making the experiment, there is some difficulty in observing the exact point at which the formation of the precipitate ceases. This difficulty is overcome by using an indicator, which consists of a little chromate of potash. If this be employed, the exact point at which the formation of chloride of silver stops will be marked by the appearance of the deep red chromate of silver.

The principle upon which the indicator depends, is that silver combines with chlorine in preference to chromic acid, and that, accordingly, no red chromate of silver is capable of being formed so long as chlorides are in the water, but that red chromate of silver instantly forms the moment the nitrate of silver is in the slightest excess.

The details of the analysis are as follows :—

70 c. c. of the sample of water is placed in a clean and white porcelain dish. A small quantity of yellow chromate of potash (about 30 milligrammes), is next placed in the water, and stirred up with a glass stirrer until it colours the water distinctly yellow. That having been done, the standard solution of nitrate of silver, which should be contained by a

properly graduated pipette, is carefully dropped into the water, which is stirred during this operation. The addition of the silver solution is continued until the red colour, which forms as the silver solution touches the water, becomes permanent on stirring. The very earliest point at which the chromate of silver becomes persistent should be read.

Certain precautions ought to be taken in performing these operations. The necessity of the chromate of potash being free from chlorides is almost too obvious to require mention. Suffice it to add, that there is now no difficulty in meeting with this substance in a state of sufficient purity in commerce. Neither the nitrate of silver nor the sample of water should be acid. If, as occasionally happens, the water be acid, it may be neutralised with pure carbonate of soda; or, indeed, it may be rendered faintly alkaline with advantage.

The reason why acidity has to be avoided is that chromate of silver is dissolved by acids; and in the determination of chlorine it is my practice, after having noted down the exact point at which the liquid becomes red, to run in about one cubic centimetre of the silver solution, in order to make sure that there is no free acid. A very proper precaution to take is to make a blank trial with distilled water, and also a trial with water containing a known quantity of chlorine, before beginning the analysis. As has been above directed, the quantity of water to be taken for the determination of chlorine is 70 c. c. This is the miniature gallon in which the milligramme is the representation of the grain. If then we know the number of cubic centimetres of silver solution which is required in order to use up all the chlorine, we know the number of milligrammes of chlorine in the 70 c. c. of water; and consequently we know the number of grains of chlorine in a gallon of the water.

As will be found on actually trying this process, this determination of chlorine is made with great facility and rapidity. For most purposes sufficient accuracy is secured if the operation be performed on the small scale above described, and, as will be found, the error of experiment may be easily limited to 0·1 cub. cent., even when so little as 70 c. c. of water is operated upon. If a higher degree of accuracy be desired, it may be attained by taking double or treble that quantity of water, and evaporating it down to a small bulk before proceeding with the titration.

By way of example, we give the following table of the chlorine in a number of samples of water :—

	Grains of chlorine per gallon.
Bala Lake (*Wales*)	0·7
Ullswater (*Cumberland*)	0·7
Thames at Kew	0·8
Thames' Companies in London	1·2
New River Company, London	1·1
Guildford, New Water Supply (*Surrey*)	0·9
Leek (*Staffordshire*), Town Water	0·7
Leek (*Staffordshire*), Workhouse Well	0·5
Tunbridge Wells	3·7
London—Pump in Portland Place	2·2
„ Pump in Goodge Street	12·4
„ Pump in Oxford Market	33·2
Well in Windsor	6·9
Sample of Sewage	9·9

CHAPTER IV.

ORGANIC MATTER—FREE, AND "ALBUMINOID" AMMONIA.

The determinations of solids and of chlorine, described in the preceding chapters, are only of secondary importance in comparison with determinations of organic matter in drinking water; and it is to the latter that the water-analyst should chiefly direct his attention.

The earliest method of estimating the organic matter was by the loss on ignition. The solid residue got on evaporating a given volume of water to dryness, was carefully dried, weighed, ignited, and again weighed; and the difference in weight before and after ignition was taken to represent organic matter. To this procedure there are very many objections. The loss on ignition, besides including the amount of organic matter dissipated or burnt during the ignition, included much else. There was loss of carbonic acid from the carbonate of lime, and loss of water when a hydrated salt, such as sulphate of lime, became an anhydrous salt, and there was loss of acid from magnesian salts, if they happened to be present in the solid residue. An attempt was made to get over these difficulties by the employment of a small and known weight of carbonate of soda, which was put into the water before evaporation to dryness, and the weight of which was afterwards subtracted from the weight of the water-residue. The loss of carbonic acid from the carbonate of lime was repaired, by careful treatment, with solution of carbonic acid and re-drying at 130° C. By these devices, as those can testify who have worked the process, it was quite possible to get very constant results; but having got the results, new difficulties started up, and it was shown that there still remained the loss in weight, occasioned by the destruction and dissipation of the nitric acid which exists in considerable quantities in most drinking-waters. When a water-residue is ignited, it loses nitric acid, and gains the equivalent of carbonic acid; and the loss in weight involved by this exchange is far-larger than the organic matter. In consequence of the adoption of the ignition-process for the estimation of the amount of organic matter in water, a very exaggerated estimate of quantity of organic matter actually present in waters used to prevail among chemists. Thus the organic matter, as determined by this process in the water supplied by the Thames' Companies to London, was from 15· to 17· parts per million (or a little over one grain per gallon). The water of the Kent Company, which is now known to be all but absolutely devoid of organic matter, showed, in like manner, a loss on ignition amounting to 16·5 parts per million. In truth, however, these numbers do not so much represent organic matter as exchange of nitric acid for its equivalent of carbonic acid; and chemists have been agreed for some years in rejecting the ignition-process in the estimation of the organic matter in drinking-water.

The next process which was tried was the permanganate process. A dilute solution of permanganate of potash, of ascertained strength, was prepared. To a given volume of the water to be tested, this standard solution of permanganate was added as long as it was decolourised by the water. From the quantity of permanganate destroyed, the quantity of oxygen taken up by the water could be calculated, and waters could be compared together as to their deoxidising powers. This process was a great advance on the ignition process, but still it did not prove to be satisfactory, and has been to a great extent abandoned. One of its striking advantages over the combustion process was that the preliminary evaporation to complete dryness (which risks loss and destruction of organic matter) was altogether avoided. The defects of the permanganate-process are its want of delicacy, and also the circumstance that albumen is not readily attacked by the standard solution of the permanganate.

The next process which we shall mention is very unsatisfactory in every way. Instead of estimating the organic matter by loss on ignition, an attempt was made to perform an organic analysis of the dry water-residue, and to determine the carbonic acid and nitrogen resulting from its combustion, with excess of oxide of copper and chromate of lead. This method was proposed by Dr Frankland, and brought out by Drs Frankland and Armstrong in the year 1868, and an account of it may be found in the Journal of the Chemical Society for that year. To a great extent it was a going back to the errors of the earliest method. There was the risk of destroying the organic matter during the evaporation to dryness in the water-bath. The nitric acid, which was one of the great sources of difficulty in the ignition-process, remained a source of difficulty in Frankland and Armstrong's process. As may be seen, on referring to the account of the process in the Journal of the Chemical Society, Frankland and Armstrong sought to destroy the nitrates by means of sulphurous acid applied to the water during its evaporation to dryness. It is true that the nitric acid may be utterly destroyed in that manner, but it is only too plain that that cannot be done without destruction of the organic matter; so that the analyst who should attempt to work the Frankland and Armstrong process is placed in the dilemma of either leaving nitrates in the water-residue, or else of destroying the organic matter before making the combustion.

The circumstance that the amount of nitric acid far exceeds the organic matter, imparts special importance to this difficulty.

Another fatal difficulty of the process depended upon the minuteness of the organic matter in drinking-water. The quantity of organic matter in a litre of water (and that is the quantity which Frankland and Armstrong evaporated to dryness to yield the water-residue for one analysis) is too little to admit of an organic analysis. Frankland and Armstrong have published some determinations of organic matter in a litre of water, and exhibit a greater experimental error than the total quantities which occur in water of average goodness.

In short, the process is thoroughly untrustworthy, and being also very difficult and costly, has not met with general acceptance.

The methods of determining the organic matter which we have just described are methods of the past, and have only an historical interest. We next pass on to the method which is now in general use among chemists, and which is known as the ammonia-process, giving, as characteristic data, the "Free ammonia" and "Albuminoid ammonia" yielded by waters.

This method dates back to the year 1867, when it was brought out by Smith and ourselves in a paper read before the Chemical Society on the 20th of June in that year. In its earliest form it was described in that paper, which was published later, in the year 1867, in the Journal of the Chemical Society. As originally described, there were two distinct modifications of the process, and at the time of the publication of that paper, the precise distinctions between the two modifications were little understood. Later in the year 1867 a second paper bearing on the subject was read; and in the spring of 1868, further researches bearing on the subject were published by us in the Journal of the Chemical Society, and the first edition of this treatise was published. Except the ammonia-process, there never was a new method of analysis which, within a week or two of its discovery, at once assumed its definite form—a form to which many thousands of analyses brought no essential modification. On the 20th of June 1867, two varieties of the water-process were described, and preference was given to one of them; and to-day, after many thousands of these analyses have been made by many chemists in all parts of the world, the method of operation is still the process to which preference was given in 1867; and the method which we are about to describe differs in *no essential* particular from that described in 1867.

The ammonia-process, like the permanganate-process above described—and as every adequate method for the determination of its organic matter in water must do—operates on the water itself, and not on the residue got on evaporation. The principle of the method is measurement of the nitrogenous organic matter in waters by the quantities of ammonia yielded by the destruction of the organic matter. For the measurement of the quantities of ammonia, the very delicate Nessler test is utilised. The agents used for the destruction of the organic matter are permanganate of potash, and enormous excess of caustic potash, and moreover the destruction is effected at the boiling point of the solution.

A very laborious investigation, carried out by ourselves in the year 1868 (*vide* Journal of the Chemical Society, May 1868), showed the wide applicability of the process, and justifies the conclusion that the ammonia-process, under the form in which we use it, is adequate to the measurement of the nitrogenous organic substances which occur in drinking-water. In the ammonia-process we have in fact a sort of combustion process with ammonia for the ultimate product, the peculiarity of the combustion being that it takes place in presence of the half, or a quarter of a litre of water.

The details of the ammonia-process will now be given.

The following chemicals and apparatus are required for the performances of the analyses :—

1. The Nessler Reagent.
2. Dilute standard solution of Ammonia.
3. Solution of Potash and Permanganate of Potash.
4. Carbonate of Soda.
5. Distilled Water.
6. Retort.
7. Liebig's Condenser.
8. Lamp and Retort Holder.
9. Glass Cylinders for Nessler test, or Nessler glasses.
10. Half-litre flask.
11. Measure for Solution of Potash and Permanganate of Potash.
12. Graduated Burette.
13. Pipette for Nessler Reagent.
14. Bottles, &c.

(1) *The Nessler Reagent* consists of a solution of iodide of

potassium saturated with periodide of mercury, and rendered powerfully alkaline with potash or soda. It is prepared by taking 35 grammes of iodide of potassium and 13 grammes of corrosive sublimate, and about 800 c. c. of water. The materials are then heated to boiling, and stirred up until the salts dissolve. That having been accomplished, a cold saturated solution of corrosive sublimate in water is cautiously added until the red periodide of mercury, which is produced as each drop of the solution falls into the liquid, just begins to be permanent. In this manner we obtain the solution of iodide of potassium saturated with periodide of mercury, and it remains to render it sufficiently alkaline, and to render it sensitive. This is accomplished by adding 160 grammes of solid caustic potash, or 120 grammes of caustic soda, to the liquid, which is afterwards to be diluted with water, so that the whole volume of the solution may equal one litre. In order to render the Nessler reagent sensitive, it is mixed finally with a little more cold saturated solution of corrosive sublimate, and allowed to settle.

When properly prepared, the Nessler reagent has a slightly yellowish tint. If it be perfectly white, it is sure not to be sensitive ; and requires a further addition of solution of corrosive sublimate in order to render it sensitive. Before being employed, it should be tested to ascertain its condition. For this purpose about 2 c. c. of the Nessler reagent are dropped into a very weak solution of ammonia (strength about 0·05 milligram of NH_3 in 50 c. c. of water), and if it be in proper condition, it will *at once* strike a yellowish brown tint with the solution.

The stock of Nessler reagent should be kept in a well stoppered bottle, from which a little is poured out from time to time into a smaller bottle used to contain the Nessler reagent, which is about to be used.

(2) *Dilute standard solution of Ammonia.*—It will be found convenient to keep two solutions, a stronger solution and a weaker solution. The stronger solution is made by dissolving 3·15 grammes of chloride of ammonium in one litre of distilled water. (The commercial sal ammoniac, in dry fibrous crystals, answers very well for the purpose.) If the solution be prepared, as has just been described, it will contain one milligramme of ammonia in one cubic centimetre of solution. The weaker solution is prepared by diluting the stronger one with 99 times its volume of distilled water. The weaker solution, which therefore contains $\frac{1}{100}$ milligramme of ammonia in one cubic centimetre, is generally useful.

(3) *The solution of Potash and Permanganate of Potash* is made by dissolving 200 grammes of solid potash and 8 grammes of crystallised permanganate of potash in a litre of water. The solution is boiled for some time, in order to get rid of all traces of ammonia and organic nitrogenous matter; and after about one quarter of the liquid has boiled off, it may be filled up with pure distilled water, so as to bring the solution up to the litre. Each water-analysis requires 50 c. c. of the solution; wherefore each analysis consumes 10 grammes of potash and 0·4 grammes of permanganate.

(4) *Carbonate of Soda.*—A saturated solution of carbonate of soda may be prepared by boiling an excess of the common carbonate with water; and about 10 c. c. of the solid saturated aqueous solution is the proper quantity to use in a water-analysis. Instead of solution, the recently ignited solid carbonate may be employed. The object of the carbonate of soda is to expel the free ammonia from water which is acid. It is, however, as a rule, not necessary to employ it.

(5) *Distilled Water.*—This is required for the making up of the various standards of ammonia, as will presently be explained. It must be very free from ammonia; so nearly free that in 100 c. c. of it there is not ·005 milligramme of ammonia. Such water is not to be bought; but has to be prepared by the water-analyst expressly for the purpose. A good river or spring-water is distilled in a clean retort or still, and the first portions of distillate are rejected. By and by water will distil over in a state of sufficient purity. The distillation must not be pushed too far, otherwise the latter portions of the distilled water may contain ammonia. In my own laboratory I make the same retort and condenser serve for the preparation of distilled water, and for the performance of water-analysis.

(6) *Retort.*—The size of retort which is suitable for water-analysis holds rather more than a litre when it is quite full. The retorts should be tubulated, and may be either corked or stoppered; the latter, however, seems preferable.

(7) *The Liebig's Condenser.*—A large condenser will be found to be suitable. In my own laboratory I use a large copper condenser, 60 centimetres long, and 7 centimetres in diameter; the glass tube which passes through it having a diameter of about 3 centimetres, and a length of about 90 centimetres. As will be perceived, the glass tube of the condenser is wide enough to admit of the beak of the retort entering it, without being drawn out by the blow-pipe. The most convenient packing is a little writing paper, which is wrapped round the neck of the retort where it enters the tube of the condenser.

(8) *Lamp and Retort Holder.*—A large Bunsen burner affords a convenient source of heat during the distillation. As will be explained, we apply the naked flame to the retort. The

retort-holder should be very steady and massive. We are in the habit of using a very well-known description of clamp made of metal, and lined with cork where it clips the neck of the retort. The incline of the retort-holder must be carefully adjusted to the incline of the condenser, so that the retort may be retained in position without any unnecessary pressure. The employment of a ring to support the retort from below is not to be recommended. Much of the ease of the working of the process depends upon the proper mounting of the retort, which ought to admit of the easy removal of the retort, and easy remounting of it.

(9) *Glass Cylinders for Nessler test, or Nessler glasses.*—These should be of perfectly white glass. In my own laboratory the Nessler glasses are cylinders, 17 centimetres in height and 4 centimetres in diameter. They are marked with a file-mark at 50 c. c. capacity. From half a dozen to a dozen are necessary. I use also a white porcelain tile for them to stand upon when they are used.

(10) *A half-litre flask* to measure out the sample of water is required. It should never be used for organic fluids, and indeed it is best to keep it exclusively for water.

(11) *The measure for solution of Potash and Permanganate of Potash* is a convenient glass, with a simple mark at 50 c. c. capacity. To pour well is an essential qualification that such a glass should possess. I am in the habit of using a thick glass vessel, which is an apothecaries' dispensing four-ounce measure, and which I bought in an ungraduated state.

(12) *A Graduated Burette*, divided accurately into cubic centimetres, and provided with a glass stopcock, is used for measuring out the dilute standard ammonia. It is held by any convenient holder.

(13) *The Pipette for Nessler Reagent* is made of a piece of glass tube, and requires just one file-mark at the 2 c. c. capacity.

(14) *Bottles* are required to hold the different solutions. It is of importance that the bottle holding the solution of potash and permanganate of potash should pour well. A large glass funnel is also required.

The convenience of having a water-supply and sink close at hand will be readily appreciated. It will also be found to be advantageous to keep a table, or part of a table, appropriated exclusively to water-analysis, and to appropriate a set of apparatus to it. Thus the funnel, the half-litre flask, the retort and condenser, burette, pipette, and Nessler glasses, should not be used for anything else but water-analysis.

One very important matter in testing of this order of delicacy is the cleaning and washing out of the apparatus, and it should be borne in mind that all glass surfaces which have been exposed to the air for any length of time are liable to contract traces of ammonia from the air; and the rule which has to be observed, in order to ensure accuracy, is to wash out with clean water immediately before use. Furthermore, it may be remarked that for these washings it is unnecessary to employ distilled water; and that the ordinary town-water is, as a rule, everything that can be desired for the purpose. There should, however, be no stint of the quantity of water. The analysis is performed in the following manner :—

The retort having been washed out with a little strong acid (either hydrochloric or sulphuric acid), is then washed out with good tap-water, until the few drops which drain out do not taste acid. It is then mounted in its holder, and properly connected with the Liebig's condenser, either by means of a wide india-rubber tube, or else it is just packed into the condenser by means of a little writing paper. Half a litre of the sample of water is next measured in the half-litre flask, and poured into the retort through a large funnel kept specially for the purpose. Then the stopper or cork, which must be kept scrupulously clean, is put into its place in the retort, and the Bunsen lamp is lighted, and the flame applied externally to the naked retort. The retort must be thrust right down into the flame, which, however, must not play upon the surface of the retort higher than the level of the liquid within the retort. In a few minutes the contents of the retort will begin to boil, and the water will begin to distil over. The distillate is to be collected in the glass cylinders for the Nessler test.

When 50 c. c. of distillate have distilled over, the cylinder is to be changed. The first 50 c. c. should then be *Nesslerised*, which will be explained further on. The distillation is to be continued until 150 c. c. have come over, and the 150 c. c. of distillate is to be thrown away. Having done so, and thereby reduced the contents of the retort from 500 c. c. (the quantity originally taken) to 300 c. c., the distillation is stopped for a moment.

Fifty cubic centimetres of the solution of potash and permanganate of potash, which has been described, is then to be poured into the retort through a wide funnel, and the distillation proceeded with.

At this stage of the operation it is sometimes necessary to shake the retort gently, in order to avoid bumping. This is especially the case in the analysis of very bad water. With a little practice, and a little presence of mind, the operator will very easily overcome difficulties of this description. The distillation must be continued until 50 c. c. of distillate have come over, and this must be collected in a cylinder for Nesslerising. A second 50 c. c. must be collected in another Nessler cylinder, and a third 50 c. c. must be collected; and that having been done the distillation may be stopped, and the apparatus left standing until it is required for another analysis.

Nesslerising, which has been mentioned in the above passage, is the operation of finding the strength of dilute solutions of ammonia by help of the Nessler test—a test discovered by a chemist named Nessler. The preparation of the Nessler reagent has already been described in detail. Let it be required to tell how much ammonia is present in 50 c. c. of distillate contained in one of the cylinders above mentioned.

For this purpose 2 c. c. of Nessler reagent are dropped into the 50 c. c. of distillate. This is best done by aid of the appropriate 2 c. c. pipette above mentioned. The pipette also serves as a convenient stirrer, to stir up the liquid after the addition of the Nessler reagent to it. If the 50 c. c. of distillate contain any ammonia, it will soon after the addition of the Nessler reagent, as just described, assume a rich brown colour; and the more the ammonia, the deeper the colour.

The next step is to imitate the depth of colour given by the distillate. In order to do so, a clean cylinder is taken, and into it is dropped a certain measured volume of the standard solution of weak ammonia, which is filled up with distilled water to the 50 c. c. mark on the cylinder. Two cub. cent. of Nessler reagent is then dropped into it by means of the pipette, and the whole is very thoroughly stirred up. The 50 c. c. of distillate in its appropriate cylinder, and the

50 c. c. of water containing the standard ammonia, are then placed side by side on a white surface (a white porcelain tile answers very well), and carefully looked through, and a judgment is arrived at as to which is of the deeper colour. If they be of equal depth, the Nesslerising is accomplished, inasmuch as the quantity of ammonia required to imitate the colour, which Nessler reagent imparts to the distillate, is the quantity of ammonia in the distillate. If the two solutions be not of equal depth, another standard must be made up with water, dilute standard ammonia, and Nessler reagent, and another comparison must be made.

With a little practice Nesslerising becomes very easy.

In the course of a water-analysis it will be perceived that ammonia is to be looked for at two stages; firstly, before the addition of the potash and permanganate, and secondly, after the addition of the potash and permanganate. The ammonia which comes over in the first stage is the "free ammonia," and that which comes over in the second stage is the "albuminoid ammonia."

The recommendation has been given to Nesslerise only the first 50 c. c. of free ammonia, and to throw away the next 150 c. c. Formerly it was our custom to Nesslerise all four 50 c. c. of free ammonia; but that was a useless trouble, inasmuch as the first 50 c. c. invariably contains three-quarters of the total amount of free ammonia. The rule is, therefore, to Nesslerise the first 50 c. c. of free ammonia, and then to add one-third. Thus, if in the first 50 c. c. of distillate the quantity of ammonia were found to be 0·02 milligramme, the total free ammonia would be 0·027 milligramme.

In the instance of the albuminoid ammonia, it is necessary to Nesslerise each separate 50 c. c. of distillate, and to add the amount together, in order to arrive at the total albuminoid ammonia.

Since half a litre of water is taken for the analysis, the results must be multiplied by two, in order to make them count upon the litre ; and if that be done, we shall then have the "free ammonia" and "albuminoid ammonia" expressed in milligrammes per litre, or in parts per million (which is the same thing).

The following example of the manner in which the notes of a water-analysis are kept in the laboratory may be useful.

Half a litre of water was taken for analysis.

Free ammonia . .	·01	milligrammes
(Correction) . .	·003	„
	·013	
Albuminoid ammonia .	·035	„
„ . .	·015	„
„ . .	·000	„
	·05	

Therefore, in litre—Free ammonia . =·026
Albuminoid ammonia=·10

The following analyses done by ourselves on various occasions may be cited in illustration of the results to be looked for. We have found the water of the River Thames, as supplied by the various companies, as follows :—

		(Parts per million milligrammes per litre.) Ammonia.	
Date.		Free.	Albuminoid.
1867.			
July	West Middlesex Water Co. .	·01	·07
„	„ „ .	·01	·06
„	„ „ .	·01	·06
„	„ „ .	·01	·06
1868.			
July 29.	„ „ .	·01	09

Date.		(Parts per million= milligramme per litre.) Ammonia.	
		Free.	Albuminoid.
1872.			
Oct. 3.	West Middlesex Water Co.	·01	·07
Dec. 3.	„ „ „	·00	·10
1873.			
Jan. 2.	„ „ „	·00	·08
1867.			
July	Grand Junction Company	·01	·08
„	„ „ „	·01	·07
„	„ „ „	·01	·07
„	„ „ „	·01	·07
1872.			
Oct. 8.	„ „ „	·00	·07
Dec. 5.	„ „ „	·00	·16
1867.			
July	Chelsea Company	·01	·07
„	„ „	·01	·10
1872.			
Oct. 5.	„ „	·00	·06
Dec. 2.	„ „	·02	·13
1867.			
July 6.	Southwark and Vauxhall	·03	·16
July 18.	„ „	·02	·12
„	„ „	·01	·15
1872.			
Feb. 7.	„ „	·01	·12
„	„ „	·01	·09
„	„ „	·01	·12
Oct. 2.	„ „	·06	·12
Oct. 12	„ „	·06	·13
„	„ „	·06	·12
Dec. 2.	„ „	·00	·18
1867.			
July 19.	Lambeth Water Company	·02	·14
„ 20.	„ „ „	·02	·15
1872.			
Feb. 7.	„ „ „	·01	·14
Oct. 9.	„ „ „	·01	·10
Dec. 2.	„ „ „	·01	·16

Three of the Thames' companies—viz., the West Middlesex, he Grand Junction, and the Chelsea, supply pure water during the summer months. During the winter months, however, the water supplied by these companies is by no means so pure as in the summer time. Two companies—viz., the Southwark and Vauxhall and the Lambeth—do not supply very pure water even in summer. The explanation of these results appears to be that, whereas the arrangements of the three first-named companies for the filtration of the water taken from the river are good, the arrangements of the Southwark and Vauxhall and of the Lambeth companies are defective. During the winter months, the filters of all the Thames' companies seem to be, in some degree, overtaxed. To make the investigation of the Thames' companies complete, we have analysed the water in the river at Hampton Court, where the supply is withdrawn from the river to feed the reservoirs of the different companies.

On July 9th, 1867, we analysed water taken from the river Thames above Hampton Court, and obtained the following results:—

	(Parts per million.)	
	Ammonia.	
	Free.	Albuminoid.
Sample I.	0·04	0·28
Sample II.	0·01	0·23

Such, then, is the raw material with which the Thames companies have to work; such is the condition of the water of the Thames before purification by the companies.

We have, likewise, made repeated analyses of the water with which the New River Company serves the inhabitants of London.

Our results are as follows:—

Date.		(Parts per million.) Ammonia.	
		Free.	Albuminoid.
1867.			
June 21.	New River Company	·02	·08
July 12.	„ „	·01	·05
„ 20.	„ „	·02	·05
Aug. 21.	„ „	·00	·06
1868.			
Jan. 25.	„ „	·02	·09
Aug. 1.	„ „	·00	·08
1872.			
Oct. 2.	„ „	·02	·08
Nov. 21. „	„ „	·01	·06

The water of the River Lea, supplied by the East London Water Company, we found as follows :—

		(Parts per million.) Ammonia.	
		Free.	Albuminoid.
1867.			
June 18.	East London Company	·03	·09
1872.			
Oct. 10.	„ „	·01	·04
Dec. 4.	„ „	·01	·18

The water which the Kent Company supplies to London, and which is derived from deep springs, is exceedingly pure, as is shown by the following analyses :—

		(Parts per million.) Ammonia.	
		Free.	Albuminoid.
1872.			
Feb. 7.	Kent Company	·01	·02
Nov. 20.	„ „	·01	·02

Even during the winter months this water preserves its character.

Leaving the metropolis, we have analysed the water supplied to a number of towns :—

		(Parts per million.) Ammonia.	
		Free.	Albuminoid.
1867.			
Aug. 19.	Manchester town water	·01	·06
,,	,, ,, ,,	·01	·06
,,	,, ,, ,,	·01	·07
Sept. 18.	Edinburgh town water	·00	·07
Oct. 3.	Glasgow (Loch Katrine) town water	·00	·08
1871.	Chester (Dee) town water	·00	·07
1871.	Scarborough (Yorkshire) town water	·01	·06
1873.			
July	Oxton (Birkenhead) town water	·00	·02
Aug.	Chelmsford (Essex) town water	·08	·02
,,	Leek (Staffordshire) town water	·00	·02
Dec.	Filde Water-works, Lytham, in Lancashire	·00	·10
1872.			
Feb.	New Supply to Guildford, Surrey	·00	·01

The following analyses of deep spring water, supplied by wells, have also been made :—

		(Parts per million.) Ammonia.	
		Free.	Albuminoid.
June 1867.	Caterham water	·04	·00
June 1867.	Cold Harbour, Dorking	·01	·00
May 1873.	Well in Frome, Somersetshire	·00	·02
Nov. ,,	Well water, Kirby Lonsdale, Westmoreland	·01	·03
,, ,,	Well at Chatham	·03	·03
,, ,,	Well, Henley-on-Thames	·02	·02

Five springs in the West of England.

July 1868.						
No. 1.	Containing	26	grs. solids	per gal.	·00	·01
No. 2.	,,	23	,,	,,	·01	·04
No. 3.	,,	20	,,	,,	·00	·01
No. 4.	,,	52	,,	,,	·00	·01
No. 5.	,,	20	,,	,,	·01	·03

Our investigations warrant the following general conclusions :—

Deep spring water (which is water that has undergone a very perfect natural filtration), is often so pure as not to yield 0·01 parts of albuminoid ammonia per million; and, unless mixed with surface water, does not yield so much as 0·05 parts of albuminoid ammonia per million.

The *filtered* water supplied by water companies, no matter whether derived from a lake, from clean mountain streams, or from defiled rivers, yields from 0·05 to 0·10 parts of albuminoid ammonia per million; and, indeed, if the filtration be efficient, approximates to 0·05.

In the case of the Filde Water-works at Lytham (the number for which is 0·10 per million), the remark may be made, that this water is not filtered by the company; and our general conclusion is that, when the number rises to 0·10, there is defective filtration.

When the filters are overtaxed, as happens in the rainy season and in the winter, water companies supply imperfectly filtered water, in which as much as from 0·10 to 0·20 parts of albuminoid ammonia is found in a million parts of the water; and it is matter of observation that diarrhœa is frequently prevalent in communities which drink such water.

We have next to consider the analytical characters of water which is not fit to drink. Certainly, the unfiltered water of the Thames, whether taken from the river at Hampton Court or at London Bridge, is unfit to drink; and certainly surface-wells, which contain excreta in a slightly altered condition, and which occasionally contain the *materies morbi* of cholera, or typhoid fever, yield undrinkable water; and certainly well-water, which is loaded with vegetable matter, is not fit to drink. Examples of all these various kinds of bad water are now given. We begin with examples of water supplied by water companies in an imperfectly filtered condition, and we end with veritable sewage.

		(Parts per million.) Ammonia.	
		Free.	Albuminoid.
Dec. 1872.	Southwark and Vauxhall Co.	·00	·18
„	Lambeth Company	·01	·16
Nov. 1873.	Great Yarmouth Water Co.	·00	·18
„	Thames, a little above Hampton Court, unfiltered	·04	·28
June 1867.	Thames at London Bridge, at two hours' flood	1·76	·35
„	High tide	1·02	·59
„	„	1·02	·56
„	„	1·02	·50
June 1873.	Well at Leek Workhouse	·02	·34
June 1867.	Great St Helen's Pump, London	3·75	·18
„	Pump in Bishopsgate St., London	7·50	·25
„	Pump in Drapers' Hall, London	6·00	·31
„	Pump in Edinburgh	·21	·29
June 1873.	Well in Windsor (containing 48·5 grs. of solids, and 5·6 grs. of chlorides per gallon)	1·20	·08
„	Well in Eton (containing 48·5 grs. of solids, and 5·6 grs. of chlorine per gallon)	·00	·84
Feb. 1872.	Effluent from Sewage	16·20	·90

From these examples it will be seen that the albuminoïd ammonia is excessive in waters which are undeniably contaminated, and in most of them it is very excessive.

The appearance of free ammonia in many of these polluted waters, is likewise a striking phenomenon, and requires a few words of comment. When the free ammonia exceeds 0·08 parts per million, it almost invariably proceeds from the fermentation of urea into carbonate of ammonia, and is a sign that the water in question consists of diluted urine in a very recent condition. In these instances the water will likewise be found to be loaded with chlorides.

Much albuminoid ammonia (which generally comes over slowly), little free ammonia, and almost entire absence of chlorides, is indicative of vegetable contamination, and is exemplified by the well at the Leek workhouse. Such water is very injurious to health.*

The analytical character, as brought out by the ammonia process, are very distinctive of good and bad waters, and are quite unmistakable. There is, indeed, hardly any branch of chemical analysis in which the operator is less exposed to the risk of failure.

As will be found on subjecting "effluent waters," and certain very bad well-waters, to analysis in the manner above described, the first 50 c. c. of distillate from the half-litre of water will be so highly ammoniacal as to yield, on Nesslerising, a colour too deep to be accurately read off, or even will yield a precipitate with the Nessler reagent. Under these circumstances, one of two obvious devices may be adopted. In order to read, by the Nessler-test, the ammoniacal strength of the 50 c. c. of distillate, which cannot be Nesslerised in its undiluted condition, we may obviously dilute it to ten times its bulk, and then (having carefully mixed up thoroughly)

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* In the Leek Workhouse there has been for years past a general tendency to diarrhœa, which could not be accounted for until the water was examined, and shown to be loaded with vegetable matter. The water was almost free from chlorine, containing only 0·5 grain per gallon. A well on Biddulph Moor, a few miles from Leek, yielded 0·5 grain chlorine per gallon, and ·03 "free" and ·14 albuminoid ammonia per million. The persons who were in the habit of drinking this water suffered from diarrhœa.

submit 50 c. c. of the diluted liquid to Nesslerisation. And, in a general way, if it be desired to Nesslerise a concentrated ammoniacal liquid, the object may be attained by first diluting to a known extent, and then Nesslerising, and making a perfectly obvious calculation.

Another method of dealing with sewages, "effluents," and bad well-waters, is by diminution of the quantity to be operated upon; instead of a half-litre we may take 100 c. c., or even less. For this purpose, half a litre of freshly-distilled water is placed in the retort, and distilled until 50 c. c. of distillate have come over (this must not contain more than ·01 or ·02 milligram of NH_3), and then, everything remaining *in situ*, and the whole apparatus being thus in a condition of guaranteed freedom from ammonia, the 100 c. c. of bad water may be dropped directly into the retort, and the operation proceeded with in the usual manner. In these cases the addition of carbonate of soda will generally be called for, and this substance should be freshly ignited before being employed.

APPENDIX.

When the ammonia-process was first brought out, the quantity of water taken for analysis was one litre, but it was very soon found that a half-litre was a sufficient quantity for most practical purposes, and that, all things considered, that was the most convenient quantity to be taken. The degree of accuracy with which the Nesslerisings were made was within half a hundredth of a milligramme.

I have, however, found that, with suitable apparatus and precautions, an accurate analysis of 100 c. c. of water may be made, the Nesslerising being, in this instance, done to within one thousandth of a milligramme.

I have analysed the same water on the two scales—viz., taking a half-litre and 100 c. c. for the analysis—and got the same results.

The apparatus to be employed consists of a little retort and narrow Liebig's condenser (figured in Chapter XII., being the same which is used in the analysis of urine). The above-described solution of potash and permanganate of potash (strength 200 grammes of solid potash and 8 grammes of crystals of permanganate of potash to a litre of water), which has been previously boiled, so as to be absolutely free from ammonia and nitrogenous organic matter, is employed.

The operation is managed as follows:—

Firstly, The retort and condenser are to be made scrupulously clean, and are to be guaranteed as being clean. This is done by mounting the apparatus, charging the retort with 100 c. c. of tolerable drinking-water, and with 10 c. c. of the permanganate solution, and distilling till the distillate comes over clean—*i.e.*, free from ammonia. That being accomplished (and such a preliminary is absolutely necessary), we may proceed.

The retort is disconnected, and the solution of permanganate having been turned out, it is washed with clean tap-water, drained, and then charged with 100 c. c. of the sample to be analysed. Having been mounted and properly connected with the Liebig's condenser, the distillation is to be commenced, and when 10 c. c. have distilled over, the 10 c. c. of distillate is to be Nesslerised in a glass presently to be described. That having been done, 30 c. c. more are to be distilled off, and either Nesslerised or thrown away.

At this stage the distillation is to be interrupted, and 10 c. c. of the solution of potash and permanganate of potash are to be poured into the retort, and the operation continued so long as 10 c. c. of distillate shows a sign of ammonia.

The Nesslerising in these delicate operations is managed in glasses of thin, white glass, cylindrical in form, 10 centimetres long, and 15 centimetres broad, and closed at one end, so as to stand upright on a white porcelain tile. The charge of Nessler reagent is to be about 0·5 c. c. (instead of 2 c. c. as when working on the usual scale). It will, of course, be understood that $\frac{1}{1000}$ milligramme of ammonia is contained in 0·1 c. c. of the dilute standard solution of ammonia, and that the standard ammonia solution will require to be measured to the 0·1 c. c. in a suitable burette or pipette. The operator will not fail to notice that he will have no difficulty in distinguising between $\frac{1}{1000}$ and $\frac{2}{1000}$ milligramme of ammonia in these little glasses, and that the colouration is particularly visible in the meniscus of the liquid.

In conclusion, a very obvious application of this delicate process may be referred to. If one litre of a given water (and it should be a tolerably pure specimen of water) be operated upon, the distillates may subsequently be submitted to distillation in the little apparatus, and so measurements of ammonia to the thousandth of a milligramme may be effected. In this manner, a litre (or a million milligrammes) of water will yield ammonia which is measured to the $\frac{1}{1000}$ milligramme, and in this manner distinctions may be made between waters which differ very slightly indeed in purity. I do not think that we are at present called upon to accomplish this task; but we are now ready if the need should arise.

CHAPTER V.

POISONOUS METALS.

A HIGH degree of freedom from poisonous metals is demanded of drinking-water; and a special testing for lead, copper, and even iron, forms an essential part of the usual analysis of drinking-water.

The testing may be managed very simply and expeditiously, and also very delicately, by taking advantage of the formation of dark-coloured sulphurets by means of sulphuretted hydrogen, or sulphuret of ammonium. Moreover, these metals, in very dilute solutions, do not yield precipitates of sulphuret, but yield dark-coloured solutions, the depth of which is proportional to the amount of metal present. It is, therefore, possible to estimate these metals by the depth of the colour, and I believe the first attempt to do so was made by the late Dr W. A. Miller.

The following are the details of the process, as performed in my laboratory :—

Standard solutions of lead, copper, and iron are prepared thus—

Standard solution of lead, containing one milligramme of lead in one cubic centimetre of solution, is made by dissolving 1·66 grammes of crystallised acetate of lead in one litre of water. Standard solution of copper, containing one milligramme of copper in one cubic centimetre of solution, is made by dissolving 3·93 grammes of crystallised sulphate of copper in one litre of water.

Standard solution of iron, containing one milligramme of iron in one cubic centimetre of water, is made by dissolving 4·96 grammes of crystallised protosulphate of iron in one litre of water.

In order to find how much of these metals is contained in a water, the following process may be adopted :—

For iron : into 70 c. c. of the sample of water contained in a dish of white porcelain, a glass rod, which has been dipped in sulphuret of ammonium, is to be inserted, and the water is to be well stirred up. If iron be present, the liquid will assume a dark colour, and the amount of iron may be determined by imitating the colour, by means of the standard solution of iron above described. The manner of operation will be obvious to all persons who are in the habit of measuring ammonia by the Nessler test.

Iron is not the only metal which gives a black precipitate with sulphuret of ammonium, and, as will be obvious, the getting of this black colour may be due to lead or copper, as well as to iron. The circumstance that the sulphuret of iron is dissolved by dilute acid serves to distinguish it from the sulphurets of lead and copper, which are not soluble in dilute acids; and in practice we first obtain the colouration in an alkaline solution, and then render slightly acid with a drop or two of hydrochloric acid, and observe whether or not the colour disappears or diminishes in depth. Disappearance of the colour, or even diminution of colour, on rendering acid, is a sign of the existence of iron in the liquid.

The manner of estimation of copper or lead is sufficiently obvious. The 70 c. c. of the sample of water contained in a white porcelain dish is stirred round with a glass rod, moistened with sulphuret of ammonium, and is then rendered faintly acid with hydrochloric acid, and the depth of colour observed. That having been done, 70 c. c. of distilled water, into which a certain measured quantity of standard copper-solution, or standard lead-solution, has been put, is also treated with a drop of sulphuret of ammonium, and the resulting depth of colour compared with that given by the sample of water.

Good drinking-water ought not to contain more than $\frac{1}{10}$ or $\frac{2}{10}$ grains of iron per gallon; and should contain less than $\frac{1}{10}$ grain of lead or copper. It is unnecessary to make out whether the metal be lead or copper, for either would condemn the water.

As will be found out in practice, the $\frac{1}{10}$ grain of iron, lead, or copper in one gallon of water is quite visible, even if only the miniature gallon (*i.e.*, 70 c. c. of the sample of water) be operated upon as above described. And, practically, the usual testing of potable water for metals resolves itself into the following very simple procedure:—Seventy cubic centimetres of the water are placed in a porcelain dish, and stirred up with a glass rod, moistened with sulphuret of ammonium. The observation is then made whether or not there is any colouration. If there be colouration, it should only be just visible; and on adding two or three drops of hydrochloric acid it ought to vanish absolutely. Water which answers to this test in a satisfactory manner, is registered as sufficiently free from poisonous metals; and water which does not, is to be condemned as contaminated with metallic impurity.

If a more delicate testing for the above metals be required, such may obviously be accomplished by making a preliminary concentration by evaporating the water before adding the sulphuret of ammonium; and on this subject nothing need be said, except that the evaporation is generally unnecessary, and that when it is resorted to the water should *not* be evaporated down either in a platinum dish, or in a vessel of lead-glass, but always either in a vessel of hard German glass, or else in a porcelain dish.

It occasionally happens that it is requisite to test a drinking-water for arsenic. This is done by concentrating, and afterwards introducing the concentrated water into a Marsh's apparatus, and looking out for the arsenical spots and rings.

Marsh's apparatus is a small apparatus for generating hydrogen, the exit-tube being armed with a small drying-tube containing chloride of calcium, and narrowed at its extremity, so as to permit of the hydrogen being burnt as it escapes. It consists of a small flask or bottle, containing fragments of pure zinc and some water. Through the cork, which closes the flask or bottle, a funnel-tube is passed, and also an exit-tube bent at right angles. Before being employed in testing for arsenic, it is absolutely necessary to prove that no arsenic is contained by the apparatus. This is done by pouring some sulphuric acid through the funnel into the apparatus, whereby the generation of hydrogen will be caused, and afterwards testing the hydrogen gas for arsenic as it escapes through the exit-tube. The testing of the gas for arsenic is managed by holding a piece of white porcelain in the hydrogen flame, which will deposit the well-known brown arsenical spot on the porcelain if arsenic be present. A still more delicate manner of testing for arsenic, is by heating the glass-tube through which the gas is issuing, when the presence of arsenic will be manifested by the deposit of a ring of metallic arsenic inside the tube, and just a little in advance of the hot part of the tube. In working with the Marsh's apparatus, care should be taken to avoid explosions; for if the hydrogen be lit prematurely before all the air has been displaced in the apparatus, there is danger of the well-known explosion by reason of sudden ignition of a mixture of hydrogen and air.

If the Marsh's apparatus show no arsenic when submitted to the testing just described, the concentrated water to be tested for arsenic may be introduced, and the hydrogen again tested for arsenic, as has been described.

Barium.—It is sometimes well to test for this metal, which, however, cannot be present in any waters containing the least traces of sulphates. The testing is very simple: the water is to be concentrated, and then treated with a few drops of dilute sulphuric acid, which will cause a white precipitate or turbidity if barium be present. The water-residue should also be examined as to the colour which it imparts to the flame, and the greenish barium-flame looked out for. It should also be borne in mind that lead also forms a white insoluble sulphate, which should not be mistaken for sulphate of baryta.

Zinc.—Occasionally this metal should be looked for in water. The method of detection depends on the peculiarity of zinc-compounds yielding a solution when treated with excess of potash or soda, and upon this alkaline solution yielding white sulphuret of zinc when treated with sulphuretted hydrogen.

Manganese.—This metal occurs sometimes in river-water into which manufacturers of bleaching-powder have discharged their refuse. A case in point came under my observation a few years ago in the north of England. This metal, in very minute quantities, is probably without much action on the animal economy, and at any rate we know of no action which it is said to exert. Manganese is detected in drinking-water as follows :—

A considerable quantity of the water is concentrated by evaporation, and then nearly neutralised by means of hydrochloric acid, and treated with a few drops of solution of peroxide of hydrogen (which may now be bought in London). The formation of a brown precipitate of peroxide of manganese is the sign of the presence of manganese. The test is very delicate. Having obtained the oxide of manganese as a precipitate, it is easy to convert it into green manganate of soda by ignition with a little carbonate of soda and nitre.

Chromium.—It may occasionally be necessary to look for traces of chromium, inasmuch as chromium-compounds are very poisonous, and may possibly occur in drinking-water. In order to test for chromium, a large volume of water should be evaporated to dryness and ignited, the residue may then be boiled with a little dilute hydrochloric acid and a few drops of solution of sulphurous acid. That having been done, the solution should be boiled with a slight excess of ammonia, which will precipitate any trace of chromium in the form of sesquioxide of chromium along with any oxide of iron that may happen to be present. The precipitate may be ignited with a little carbonate of soda and nitre, in order to give the characteristic yellow chromate of soda.

Separate detection of Copper and Lead.—The testing for these metals conjointly has been given above, and, as aforesaid, it usually suffices to make out whether either or both are present or absent; and the water-analyst may usually be content when he has settled that question. Occasionally, however, it will happen that the separate detection of these metals is required. Copper may be detected by evaporating to dryness a large volume of water, rendering slightly acid with hydrochloric acid, and precipitating with sulphuretted hydrogen. The precipitate is then to be got on a small filter, the filter burnt in a platinum crucible, and the resulting ash heated strongly with a drop of oil of vitrol, which will form sulphate of copper. On cooling this is to be diluted with a few drops of water, and mixed with a few drops of ammonia, which will give the well-known purple-blue colour. A further step to be taken is to evaporate off the excess of ammonia, and then to add a drop of solution of yellow prussiate of potash, which will give the red-brown ferrocyanide of copper. This last reaction for copper is excessively delicate, so much so, that even when the purple-blue given by ammonia may be inconspicuous, the red-brown ferrocyanide is often strikingly visible. When it is neatly and properly executed, this testing for copper is extremely delicate and satisfactory. *Lead* may be detected by forming the iodide of lead. From a large quantity of the sample of water, previously concentrated, the lead is first obtained in the form of sulphuret. The sulphuret is got on a filter paper, and ignited in a little porcelain crucible. The residue is treated with a few drops of nitric acid, and evaporated gently. A few drops of water and a very little iodide of potassium are added, when the yellow iodide of lead will be formed.

Touching the quantities of poisonous metals to which poisoning has been traced in drinking-water, there is the very well-known instance of the poisoning of several members of the Orleans family at Claremont. In this instance, Hofmann found one grain of lead in a gallon of the drinking-water, and the poisoning was of a very marked and extraordinary description, as is related by Dr H. Gueneau de Mussy, in the *Dublin Quarterly Journal of Medical Science*, May 1849 (No. XIV., p. 420). There can, moreover, be little doubt that dangerous consequences should be looked for from so small a proportion of lead as one-tenth of a grain per gallon of drinking-water.

As to the circumstances under which lead is to be sought, as has been already said, no analysis of water for sanitary purposes is complete without a search for lead in the very simple manner described above; and one-tenth of a grain per gallon should cause the rejection of a water.

The water of mountainous districts, especially where metals abound, as in Cumberland and Derbyshire, should be very carefully searched for metals. In deciding upon the water-supply to a town, the question of the possible presence of poisonous metals assumes great importance, since it is by no means certain that filtration is capable of removing such impurities.

In this respect metallic contamination forms the most fatal of all objections to drinking-water, and is far more difficult to remedy than organic contamination, which may be got rid of completely by proper filtration.

London has, perhaps, had a most fortunate escape in the collapse of the great scheme for bringing water to it from the lake district of Cumberland.

CHAPTER VI.

THE DRAWING UP OF REPORTS.

As has been already indicated, the proper kind of analysis of potable water, which is generally suitable for sanitary purposes, comprises determinations of solids, chlorine, free ammonia, and albuminoid ammonia, and whether or not the water contains less than one-tenth of a grain per gallon of lead and copper, and whether there is more than the least trace of iron. These data having been provided, a judgment may be pronounced as to whether the water is fit for domestic use or not.

The rules for coming to such a judgment are tolerably simple. Unless the water contain more than 40 grains of solids per gallon, no exception need be taken to the solids as such.

Five or ten grains of chlorine per gallon are not an absolute bar to the use of a water, but only a reason for suspicion under certain circumstances.

If a water yield 0·00 parts of albuminoid ammonia per million, it may be passed as organically pure, despite of much free ammonia and chlorides; and if indeed the albuminoid ammonia amount to ·02, or to less than 0·05 parts per million, the water belongs to the class of very pure water. When the albuminoid ammonia amounts to ·05, then the proportion of free ammonia becomes an element in the calculation; and I should be inclined to regard with some suspicion a water yielding a considerable quantity of free ammonia along with ·05 parts of albuminoid ammonia per million.

Free ammonia, however, being absent, or very small, a water should not be condemned unless the albuminoid ammonia reaches something like 0·10 per million. Albuminoid ammonia above 0·10 per million begins to be a very suspicious sign; and over 0·15 ought to condemn a water absolutely. The absence of chlorine, or the absence of more than one grain of chlorine per gallon, is a sign that the organic impurity is of vegetable rather than of animal origin; but it would be a great mistake to allow water highly contaminated with vegetable matter to be taken for domestic use.

The following form, the one employed in my laboratory, will be found convenient in reporting on potable water:—

DATE.	NAME AND DESCRIPTION OF THE SAMPLES OF WATER.	Grains per Gallon.		Parts per Million.	
		Solids.	Chlorine.	Free Ammonia.	Albuminoid Ammonia.
	LONDON WATER SUPPLY (Thames)............	18·5	1·2	0·01	0·06
	„ „ „ New River.........	17·7	...	0·00	0·06
	„ „ „ Kent Company ...	26·5	...	00·1	0·02
	Very bad Water. Thames Water at London Bridge	...	...	1·02	0·59

CHAPTER VII.

ANALYSIS OF THE TOTAL SOLIDS.

The part of this book intended for general use by persons engaged in making analyses for sanitary purposes, was brought to an end in the last chapter, and the remainder of the book is of a more special character.

This chapter is devoted to the composition of the total solids in drinking-water.

In giving the results of an analysis of a water-residue, it used to be the custom to state the different salts of which the water-residue was composed; but of late years a different fashion has grown up, and many chemists are now in the habit of stating the results in terms of the different metals, and in terms of the different acids or acid-radicals of which the water-residue is made up. The reason for this alteration was the perception of the fact that when a solution contains various acids, and various bases, the assignment of a particular base to a particular acid must be to a certain extent arbitrary; and that so it might come to pass that one and the same water could be made to appear different by mere tricks of statement, whilst waters which were dissimilar might be made to look tolerably similar by appropriate manipulation of the analytical results.

This objection is undoubtedly weighty; but, on the other hand, if we turn to prominent examples of the modern form of representation, we are not encouraged by them, and cannot fail to be struck by their singularly impracticable character, and by their want of perspicuity.

In Watts' Dictionary, published in 1871, under the article "Water," will be found an admirable example of the modern mode of representation, where the water-residue is most strictly and rigidly broken up into its constituent metals, and constituent acid-radicals; and from this example we may judge how much is lost and how little is to be gained by the adoption of the modern form. For general purposes I am in favour of reverting to the older form, and, by the adoption of appropriate conventions, I would propose to get over any difficulties as they may arise.

The older form of representation fulfils one essential condition, which atones for all its faults. It exhibits certain waters as containing some one greatly predominating constituent, and other waters it exhibits as containing no greatly predominating constituent, whereas the new form of representation hides and buries these fundamental facts, as is most strikingly exemplified by the tabular statement in Watts' Dictionary to which we have referred.

In sea-water the predominating constituent of the water-residue is common salt, which forms about three-quarters of the water-residue. Sea-water is, therefore, a solution of common salt, containing certain other mineral matters in subordinate quantities. But, if we turn to the table in Watts' Dictionary, this fact is not apparent, and only by study do we find it out at all.

Certain very common forms of land-water, the entire water-supply of London, for instance, yield water-residues in which carbonate of lime predominates. These waters are, in fact, very dilute solutions of carbonate of lime (held in solution by carbonic acid), all other constituents of the water-residue being collectively subordinate in quantity to the carbonate of lime; and this fundamental fact is not apparent in the table.

For general purposes we must adopt a form of representation which gives prominence to important facts such as these. In dealing with the water-residue of potable waters, it will be convenient to treat the carbonate of lime as a constituent apart from all the rest; and, so to speak, to regard these waters as dilute solutions of carbonate of lime.

Water which drains from granite, and from the igneous rocks generally, as also from the older stratified rocks and from the millstone grit, contains very little mineral matter in solution. But if such water encounter limestone or chalk, its character changes at once; and from containing less than 5 or 6 grains of solids per gallon, it at once comes to contain 16, 20, or 30 grains, the gain in solid contents consisting mainly of carbonate of lime which has entered into solution.

Now, abstraction being made of the carbonate of lime, drinking-waters, as a rule, do not exhibit very great variation in the solids contained by them.

For the determination of carbonate of lime in waters we are provided with a variety of methods, which may be made to control each other. There is the direct determination of the amount of lime in the water, which will be treated of at length by and by; there is, likewise, the determination of hardness, and there is a third method, which is, I believe, new, but which is a very obvious one. The indications afforded by these three methods enable us to fix the proportion of carbonate of lime with considerable accuracy and certainty.

The taking of hardness will be described in next chapter. Here a sketch may be given of the third method, which consists in determining the soluble and insoluble constituents of the water-residue. This is a very simple operation. 700 c. c. of the water are evaporated to dryness at 100° C. in a platinum dish, and the water-residue weighed. It is then treated with small successive portions of boiling distilled water, and the resulting solution passed through a very small filter and evaporated to dryness. The washing must be managed neatly, so as to make a very little water accomplish the washing. The filtrate is then to be evaporated to dryness in platinum in the water-bath, dried at the temperature at which the total water-residue was dried and weighed. In this way we get the amount of soluble, and the amount of insoluble, water-residue yielded by a water.

The amount of wash-water to be employed should be 35 to 70 c. c., and with neatness and in the absence of more than traces of sulphate of lime, it will be found to be possible to obtain as high a soluble-residue using 35 as using 70 c. c.

The water of the New River Company as supplied to London.—The total solids in this water appear to range from 13·6 grains per gallon to 21·0; the mean for the year 1865 being, according to Dr Frankland, 17·7 grains per gallon.

According to a recent determination in my own laboratory, the solids in this water on March 4, 1874, amounted to 20·7 grains per gallon.

The first point of interest in relation to these solids is, that they consist mainly of carbonate of lime, and that the variation in the total solids in the water is mainly due to variation in the amount of carbonate of lime which it happens to have dissolved. The 20·7 grain of solids were submitted to the action of successive small quantities of boiling water, whereupon 5·5 grains dissolved out. Hence—

Soluble salts, . . .	5·5	grains per gallon.
Insoluble (mainly $CaOCO_2$),	15·2	„ „
	20·7	

The hardness of the water was found to be 15 degrees, which, as will be explained in next chapter, signifies 14 grains of carbonate of lime, the 1 degree pertaining to the water itself.

I made likewise very careful determinations of chlorine and of sulphuric acid, and obtained these results :—

Chlorine, per gallon, ...	1·10 grains.
Sulphuric acid (SO_3), per gallon, . .	0·19 „

The amount of nitric acid in New River water has been estimated by Frankland and Armstrong on various occasions, and amounts to about 1·0 grain per gallon.

Further material for deducing the chemical history of New River water is furnished by the loss on ignition, which was carefully determined by Frankland in 1865, and is, in mean, 0·7 grains per gallon. The loss on ignition consists mainly of exchange of 2 (NO_3) for CO_3; and, as will be perceived, on making the requisite calculation, one grain per gallon of nitric acid would require a loss on ignition of a little more than 0·5 grain: wherefore the loss on ignition is an additional confirmation of the determination of nitric acid.

A further point to be determined is the following :—Is the "soluble part" of the total solids alkaline, and to what extent?

We are now in possession of materials for arriving at a tolerably certain knowledge of the mineral constituents of the New River water.

The 15·2 grains of insoluble portion contains 14 grains of carbonate of lime, the difference being made up of a little silica (according to some published analyses this amounts to 0·5 grains per gallon) and to a trace of iron, and possibly of allumina and phosphoric acid, and to a trace of organic matter retained by the carbonate of lime. Magnesia is all but absent.

The 5·5 grains of soluble salts contain no lime, and consist entirely of salts of the alkalies. They contain—

Chlorine, ...	1·1 grain.
Nitric acid (NO_3), ...	1· „
Sulphuric acid (SO_3), . . .	0·19 „

The question of the presence or absence of alkaline carbonates has not been gone into.

The Thames' water, supplied by the London Water Companies.—The highest amount of total solids found by Frankland in the water of the Thames' Companies during the year 1865 was 22·8 grains per gallon, and the lowest 13·2 grains—the mean being 18·7 grains per gallon.

In an experiment in my own laboratory, I found, on March 2d, 1874, 22·9 grains of solids per gallon; and on the 27th of March of the same year I found 21·7 grains per gallon. As in the case of the New River, these solids consist chiefly of carbonate of lime. The 22·9 grains of solids was treated with a little boiling water, and yielded up 7·8 grains.

The 21·7 grains also yielded up to boiling water 7·42 grains. And here the remark may be made that in the latter case double as much water was employed as in the former, showing the efficiency of this process.

We have, therefore—

	2d March.	27th March.	
Soluble, . . .	7·8	7·4	grains per gallon.
Insoluble, . . .	15·1	14·3	„ „
	22·9	21·7	

The hardness taken on March 27th was found to be 16·5 degrees, signifying 15·5 grains of carbonate of lime per gallon.

I have no determination of the hardness of the water-supply on March 2d, and so we must confine our attention to March 27th. On this day, at any rate, the carbonate of lime, as measured by the soap test, was larger than the insoluble residue. The meaning of this circumstance is that the soluble portion of the solid residue contains lime-salts.

We have, therefore—

Soluble salts (including lime-salts equivalent to about 1·2 grains of $CaOCO_2$),	7·4	grains per gallon.
Insoluble salts (mainly $CaOCO_2$),	14·3	„ „
	21·7	

And here attention may be called to the confirmation which is afforded by the "permanent hardness." In 1865, Frankland found the permanent hardness of Thames' water always sensibly greater than that of New River. The mean "permanent hardness" of Thames water being 4·3 degrees, that of New River was found to be 3·6 degrees. The explanation why waters sometimes exhibit a degree of hardness in advance of that which can be due to the solubility of carbonate of lime in boiled water is, that such waters contain more permanent acid than is enough to saturate the alkalies proper (*i.e.*, more hydrochloric nitric, or sulphuric acid than will saturate the potash, soda, &c., in the water).

Further determinations in Thames' water show 1·2 grains of chlorine, and about one grain of nitric acid per gallon. A recent determination of sulphuric acid showed 1·6 grains (SO_3) per gallon.

Guildford New Water-Supply.—According to an analysis of my own in 1871, this water contains 19·7 grains per gallon of solids, whereof 14·7 grains are carbonate of lime, and magnesia is almost entirely absent. In this water, therefore, there are some 4 to 5 grains of salts of the alkalies per gallon.

Determination of Lime in Drinking-water.—The usual manner in which the lime in drinking-water is determined is faulty in detail, and is not calculated to yield the most accurate results. The manner of proceeding, as is well known, is as follows:—A considerable volume of the water, having been measured or weighed out, is evaporated to dryness in a platinum dish, a little hydrochloric acid having been added, so as to impart a distinctly acid reaction. The residue is then moistened with a few drops of acid, treated with distilled water, and passed through a filter. To the filtrate excess of ammonia is added, and then the liquid is boiled and passed through a second filter. In this way silica, alumina, oxide of iron, and phosphoric acid are got rid of as precipitates, and the filtrate is next mixed with oxalate of ammonia, which throws down the oxalate of lime. This is then washed, &c.

Now, the two precipitations to remove traces, before the precipitation of the main ingredient of the water-residue, are very objectionable, and involve a sacrifice of accuracy in more ways than one.

The plan which I recommend is this. I take 700 c. c. of the water, and, having ascertained that it is quite bright, I add about half a gramme of crystals of oxalic acid, and some 2 or 3 c. c. of strong ammonia, taking care, however, to have excess of both reagents. Then I stir up and filter through a small filter, and when the filtrate has run through I wash with a very little distilled water. The filtrate is meanwhile set to evaporate down in a large platinum dish, and is evaporated to some 10 c. c. in bulk. If necessary, a drop or two of hydrochloric acid is added, and the liquid is got into a small beaker and mixed with a little ammonia, which will throw down a fresh quantity of oxalate of lime, which is got on a very little filter and washed, and the filtrate and wash-water sent through this filter should not much exceed some 30 c. c. altogether.

By this manner of operation we gain several advantages. We precipitate most of the oxalate of lime in very dilute solution, and ensure the completest washing. At the same time, by making the second minute precipitation, we avoid the great disadvantage of complete washing—viz., loss of some of the precipitate in virtue of its solubility. Inasmuch as the second precipitate is very small in quantity, and in very little bulk of liquid, we can make a very minute filter serve to retain it, and can make a very little wash-water serve to wash it several times.

The question of the carrying down of silica, &c., along with the oxalate of lime, is best reserved, and after the oxalate has been converted into carbonate of lime, or into sulphate of lime, and weighed, a correction may be made, if necessary, for traces of these substances.

Magnesia.—There can be little doubt that the magnesia in drinking-water is, as a rule, very badly determined. The second precipitate of oxalate of lime is, in the ordinary way of analysis, very apt to be confounded with the magnesia. The only special directions which I have to give are, that having separated the second precipitate of oxalate of lime, the filtrate, which is small in volume, is to be mixed with a slight excess of phosphate of soda and a considerable quantity of strong liquor-ammoniæ, left to stand, and the resulting ammonia-phosphate washed, dried, ignited, and weighed.

Alkalies.—Evaporate a considerable bulk of water down to dryness in platinum in the water-bath; treat the residue with a little boiling water, filter and wash; treat the filtrate with a slight excess of baryta-water (to precipitate magnesia), filter, concentrate in platinum, and then precipitate with a little carbonate of ammonia (to remove baryta and lime), filter and evaporate the filtrate to dryness, ignite gently, and weigh. Notice whether the weighed residue is sensibly alkaline, and if it be so, acidify with a drop of hydrochloric acid and water, dry down in the water-bath, heat to low redness, and weigh. The alkalies will be in a state of chlorides, and may be further investigated in various obvious ways.

CHAPTER VIII.

HARDNESS.

It is matter of the commonest observation that the water in different places differs in hardness or softness. It is hard if much soap be required in order to make a lather, and soft if little soap be required. These differences depend upon the presence of compounds (generally lime- or magnesia-salts) which decompose the soap. The more lime or magnesia in the sample of water, the more soap a given volume of the water will decompose so as to give insoluble oleate, palmitate and stearate of lime or magnesia, and consequently the more soap must be added to a gallon of water, in order that the necessary quantity of soap may remain in solution, so as to give rise to the phenomenon called lathering.

Many years ago the late Dr Clark brought out a simple method of measuring the degree of hardness of different waters. He ascertained, by direct trial, how many measures of a standard solution of soap were required by a gallon of water, in order to form a lather. Nothing could be more simple or more direct than Dr Clark's soap-test in itself, but unfortunately an unhappy mode of registering the results was adopted, and a certain degree of confusion crept into this transparently simple matter.

Instead of registering the degree of hardness of a water as the number of measures of standard soap-solution consumed in producing a lather, he registered the degree of hardness as the number of grains of carbonate of lime (or its equivalent of other soap-destroying salts) in the gallon of water.

That a certain definite quantity of soap—and not an infinitesimally small quantity—must be required by a gallon of distilled water in order to produce a permanent lather, is a perfectly obvious fact when it is pointed out. This fact was, indeed, recognised by Dr Clark, who, although aware of it, had not realised all its consequences, and has thereby fallen into a little confusion. This question is fully discussed in the Appendix, to which the reader may be referred.

Since the first edition of this book was written, we have adopted the perfectly direct and simple method of registering degrees of hardness. The relative degrees of hardness of two waters are, on our scale, simply the number of soap-measures consumed by a gallon of the waters in yielding a permanent lather; and the quantity of soap in one soap-measure is the quantity required to precipitate one grain of carbonate of lime.

A gallon of water is an unwieldy quantity to work with. We therefore (and Dr Clark did similarly) employ, in practice, a much smaller volume, and a correspondingly small fraction of the quantity of soap in the measure of standard soap-solution. We take our miniature gallon, viz., 70 c. c. of water. This, as has been often explained, contains as many milligrammes of water as there are grains in a gallon. Our standard soap solution is made to contain exactly sufficient soap in one cubic centimetre to precipitate one milligramme of carbonate of lime. When, therefore, we use the miniature gallon, and a certain number of cubic centimetres of standard soap solution, it is as if we had taken an actual gallon of water, and tested it with a certain number of measures of standard soap-solution, whereof each measure contained soap equivalent to one grain of carbonate of lime.

The operation of measuring the degree of hardness of water is very simple.

Into a stoppered bottle (capacity about 200 c. c., but exact size of little importance), which has been cleaned and rinsed with distilled water, 70 c. c. of the sample of water is to be poured. The stopper is put into its place, and the bottle is shaken up. That having been done, the standard soap-solution is to be measured into the water by means of a burette or pipette graduated into cubic centimetres. After each addition of the soap-solution, the bottle containing the water is to be shaken up, and the point is by and by noted when a lather forms.

In order to observe the formation of the lather, the bottle should be laid on its side; and the lather, to be satisfactory, must be capable of *persisting* for five minutes.

In practice, if nothing be known about the degree of hardness of the sample, it will be found to be most convenient to run in the soap-solution boldly, 5 c. c. at a time, and make out approximately and rapidly the degree of hardness of the water. Having done so, in a second more careful experiment the soap-solution is at once run in almost up to the required quantity; and then small additions of the soap-solution are carefully made, and the exact state of the lathering carefully observed after each addition.

In this manner the taking of the degree of hardness is easily and rapidly accomplished.

In cases of very hard water, when the hardness exceeds 16 degrees, a dilution with distilled water is required, in order that the lathering may take place regularly. If, then, after the addition of 16 c. c. of the soap-solution no lather be formed, 70 c. c. of distilled water must be poured into the bottle, and the addition of the standard solution proceeded with. But afterwards, in writing down the degree of hardness, an allowance of one degree must be made for the addition of the 70 c. c. of distilled water.

Another method of effecting the same object is by diluting a hard water with once, twice, &c., times its volume of distilled water, and then titrating the diluted water by means of the standard soap-solution. And in such cases the number of cubic centimetres of soap-solution must be multiplied by two, three, &c., as the case may be.

The reasons why this dilution is called for appear to be that too large a proportion of insoluble lime-salts interferes with the lathering, and also that if more than 16 c. c. of alcoholic solution of soap go into 70 c. c. of water, the proportion of alcohol becomes too high to admit of satisfactory lathering. The rule is, therefore, that water must be diluted appropriately, so that 70 c. c. should never take more than 16 c. c. of soap-solution.

Preparation of the Standard Solution of Soap.—I have met with a very convenient soap for this purpose. It is green Castile soap, and is described as containing 60 per cent. of olive oil. It is now abundant in London. If 10 grammes of the soap be dissolved in a litre of weak alcohol, it yields a solution containing exactly sufficient soap in one cubic centimetre to precipitate one milligramme of carbonate of lime.

The standard soap-solution is therefore prepared by dissolving 10 grammes of this kind of soap in a litre of weak alcohol, which may conveniently be of about 35 per cent. in strength. Care must of course be taken to dissolve all the soap; filtration must not be resorted to, and if the soap-solution be turbid, it must simply be shaken up before being used.

The strength of the standard soap-solution may be verified by means of a solution containing a known quantity of carbonate of lime, or of chloride of calcium equivalent to a known quantity of carbonate of lime.

This may be prepared as follows:—1·11 gramme of pure fused chloride of calcium is dissolved in a litre of water. This solution contains chloride of calcium at the rate of one milligramme of carbonate of lime in one cubic centimetre.

In order to verify the soap-solution, a number of cubic centimetres of this standard solution of lime—say 12 c. c.—is to be put into the 70 c. c. measure, and filled up to the 70 c. c. mark. In this way 70 c. c. of water are made to contain lime equivalent to 12 milligrammes of carbonate of lime. The 70 c. c. of distilled water itself consumes soap equivalent to one milligramme of carbonate of lime in forming a lather. Therefore this 70 c. c. of solution is equivalent to 13 milligrammes of carbonate of lime, and should consume exactly 13 c. c. of the standard soap-solution.

Should the soap-solution not be of right strength, it must be made either stronger or weaker until it is correct in strength.

The following determinations of hardness may be cited. They have all of them been made with my own solutions :—

Date.		Degrees of Hardness.
1874.		
March 4.	London, New River Co.,	15·0
„ 27.	London Thames Co.,	16·5
Jan. 5.	Castleton, Derbyshire,	11·0
1873.	Leek town-water,	3·8
„	Leek Workhouse Well,	5·2
„	Oxton, Birkenhead,	11·9
„	Chelmsford, Essex, town-water,	13·3
„	Cockermouth, Cumberland,	2·5
„	Kirby Shore, Westmoreland,	25·0
„	Chatham,	24·0
„	Darley Dale, Derbyshire, Well,	7·5

These hardnesses are, as has been explained, the relative volumes of standard soap-solution destroyed by a gallon of water in producing a permanent lather.

Suppose the question to arise—How much carbonate of lime is contained by a gallon of one of these waters, the answer is found by subtracting one degree (which is due to the gallon of water itself). Thus, New River water contains 14 grains of carbonate of lime, or else other salts equivalent to 14 grains of carbonate of lime. The Cockermouth water contains only 1·5 grains of carbonate of lime, or salts equivalent to 1·5 grains of carbonate of lime in the gallon.

All the above determinations are what are called determinations of total hardness. If a water charged with carbonate of lime be boiled, the excess of carbonic acid escapes, and there is deposit of more or less carbonate of lime: and consequently the water becomes softer.

The hardness of the water after this deposit is termed the *permanent* hardness, and the difference between the two is termed *temporary* hardness.

CHAPTER IX.

NITRATES, IODATES, AND CHLORATES.

Several methods are in use for the estimation of the nitrates and nitrites in water. The best method, in our opinion, is a modification of Schulze's, which has been recently described in the *Journal of the Chemical Society*.* It consists in converting the nitrates and nitrites into ammonia by means of metallic aluminium acting upon them in the cold and in strongly alkaline solution.

The process is carried out as follows:—50 c. c. of the water are introduced into a non-tubulated retort, and 50 to 70 c. c. of a solution of caustic soda added. The caustic soda must be free from nitrates, and the strength of the solution should be such that 1 litre contains 100 grm. of caustic soda. If necessary the contents of the retort may be distilled until no ammonia comes over; that is, until the Nessler test is incapable of detecting ammonia in the distillate. The retort is now cooled, and a piece of aluminium introduced into it (foil will answer very well with dilute solutions, but we much prefer thin sheet aluminium in all cases). The neck of the retort is now inclined a little upwards, and its mouth closed with a cork, through which passes the narrow end of a small tube filled with

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* Chapman, May 1868.

broken-up tobacco-pipe, wet either with water, or, better, with very dilute hydrochloric acid free from ammonia. This tube need not be more than an inch and a half long, nor larger than a goose-quill. It is connected with a second tube containing pumice-stone moistened with strong sulphuric acid. This last tube serves to prevent any ammonia from the air entering the apparatus, which is allowed to stand in this way for a few hours or over night. The contents of the pipe-clay tube are now washed into the retort with a little distilled water, and the retort adapted to a condenser, the other end of which dips beneath the surface of a little distilled water free from ammonia (about 70 to 80 c. c.)* The contents of the retort are now distilled to about half their original volume ; the distillate is made up to 150 c. c. ; 50 c. c. of this are taken out, and the Nessler test added to them. If the colour so produced be not too strong, the estimation may be made at once ; otherwise the remainder of the distillate must be diluted with the requisite quantity of water.

Should it be desired to determine the ammonia by titration (alkalimetry), a much larger quantity of the water must be employed. Half a litre or a litre should be evaporated down to a small bulk, and treated in exactly the same manner, except that the distillate is received in standard acid instead of water.

It will be understood that the purity of the reagents must be ascertained by making blank experiments. We have met with common caustic soda, sold in lump, which has proved to

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* Condensers are very apt to obtain a trace of ammonia if they have been standing all night, and must, therefore, be washed out with the utmost care. We prefer to distil a little water through them until ammonia can be no longer detected in the distillate.

be free from nitrates. Should the caustic soda be found to contain nitrates, they may be destroyed by dissolving a small quantity of aluminium in the cold aqueous solution, and the resulting ammonia should afterwards be expelled by boiling. By dissolving metallic sodium in distilled water, we may also very conveniently prepare soda free from nitrates. This process is specially adapted to those cases wherein the amount of nitrates is very small, and is, we believe, the only method which gives accurate results under such circumstances.

The following examples will serve to indicate the degree of trust which may be reposed in it:—

Expt.	Nitric Acid HNO_3 employed. Milligrm.			Ammonia NH_3 obtained. Milligrm.	Ammonia NH_3 theory. Milligrm.
I.	100		(alkalimetry)	27·5	27·0
II.	100		(alkalimetry)	27·8	27·0
III.	100		(Nesslerising)	25·0	27·0
IV.	100		(Nesslerising)	28·0	27·0
V.	7		„	1·80	1·89
VI.	1	(with salts)	„	0·28	0·27
VII.	1	(with salts)	„	0·26	0·27
VIII.	1	(with salts)	„	0·25	0·27
IX.	1	(with salts)	„	0·27	0·27
X.	1		„	0·25	0·27
XI.	0·5		„	0·14	0·135
XII.	0·5		„	0·12	0·135
XIII.	0·2		„	0·05	0·054
XIV.	0·3		„	0·078	0·081
XV.	0·1		„	0·025	0·027
XVI.	0·1		„	0·025	0·027

The nitric acid was taken in the form of nitrate of potash.

In experiments VI., VII., VIII., and IX., different inorganic salts were put into the water along with the nitric acid, in order to ascertain whether their presence would have any effect on the reduction of the nitric acid to ammonia. In expt. VI., 50 milligrm. of NaCl were used; in expt. VII., 50 milligrm. NaCl and 80 milligrm. K_2OSO_3; in expt. VIII., 50 milligrm. of phosphate of soda; in expt. IX., 50 milligrm. Fe_4Cl_6 and 50 milligrm. of Mg_2OSO_3. It is proved that the presence of salts has no influence on the result.

The adaptation of the method to small quantities is very well shown by the above experiments, which exhibit it as answering just as well with a few hundredths of a milligrm. as with a few milligrms. of material. This extreme delicacy is due to the fact that we are able to employ the Nessler test.

In the process, as we have just described it, there is a *distillation*. Should there be any reason for avoiding a distillation, the following modification may be used:—

Prepare a soda ley by dissolving 100 grm. of solid soda in water and diluting to a litre, and insure its freedom from nitrates by taking the soda as free from them as can be obtained in the first instance, and subsequently dissolving a very little aluminium in the cold solution of the alkali. Take 200 c. c. of this soda ley and mix it with 200 c. c. of the sample of water, and place in the mixture a bit of metallic aluminium. Allow the aluminium to dissolve in the cold, and the liquid to become clear. There will thus be got a liquid containing the original ammonia and the ammonia arising from the nitrates. Every 100 c. c. of this liquid will contain 50 c. c. of the sample of water.

For comparison take 200 c. c. of the soda ley and dissolve in it in the cold the same quantity of aluminium as before. When the aluminium has dissolved, add 200 c. c. of the sample of water, and allow to subside. Every 100 c. c. of the mixture will contain 50 c. c. of the water and 50 of soda ley. This *comparison-liquid* will be like the first one in every respect except one : whereas the first one has the nitrate reduced to ammonia, it will have the nitrates in the unreduced state. Decant and determine the ammonia by the Nessler test (see § 55, using the *comparison-liquid* instead of distilled water, and using the standard ammonia of strength 0.1 milligrm. per 1 c. c.)

It will be observed that the *comparison-liquid* contains as much *original ammonia* as the liquid which is to be compared with it, and that therefore no correction is needed for original ammonia. Before mixing the sample of water with the soda ley—whether to make the liquid to be reduced or the *comparison-liquid*—add a very little chloride of calcium, so as to get an appreciable quantity of precipitate on mixing with the soda ley.

It will be understood that when the ammonia originally present in water is large relatively to that given by the nitrates —as occasionally happens—this plan without distillation would not be advantageous.

It is of course open to the analyst to expel the free ammonia more or less completely by boiling the water before commencing the operation of determining the nitrates.

Dr Letheby finds it better in estimating nitrates by this method to employ a much larger surface of aluminium than here recommended. The operation is certainly much hastened by this course of proceeding, and provided that care be taken not to allow the liquid to get too hot during the reaction, there can be no objection. The following modification of the method has been found by us to answer well.

A tubulated retort of about 350 or 400 c. c. capacity is taken. To the tubulure is adapted a cork and safety tube.

The body of the retort is about one-third filled with scraps of aluminium. Dilute solution of potash or soda is now added through the safety tube, and the contents of the retort distilled until no ammonia can be detected in the distillate. The apparatus is now dismounted, the liquid emptied out, and the water containing the nitrate to be estimated poured in. Strong soda or potash solution, which gives no ammonia when treated with aluminium, is now poured down the safety tube in small portions at a time, so as to start a gentle evolution of hydrogen. Care must be taken that the contents of the retort do not get notably heated by too violent an action. Should this appear to be imminent, water should be added through the safety tube. When the reaction has proceeded for fifteen or twenty minutes, the reduction will be found to be complete.

The liquid contents of the retort are now transferred to another retort, the great excess of aluminium washed with a little pure water, and the washings added to the main body of the liquid. This liquid is now distilled, and the ammonia estimated in the distillate. The excess of aluminium in the first retort is ready to act on a fresh sample of water. It may be used many times in succession.

A description of Frankland and Armstrong's process is to be found in the *Journal of the Chemical Society* for 1868, page 101. We quote from that journal :—

"*Estimation of Nitrogen in the form of Nitrates and Nitrites.*—The following is the mode in which this process is applied to the estimation of nitrogen existing as nitrates and nitrites in potable waters :—The solid residue from the half litre of water used for determination, No. 1 (estimation of total solid constituents) is treated with a small quantity of distilled water ; a very slight excess of argentic sulphate is added to convert the chlorides present into sulphates, and the filtered liquid is then consecrated by evaporation in a small beaker, until it is reduced in bulk to two or three cubic centimetres. The liquid must now be transferred to a glass tube, furnished at its upper extremity with a cup and stopcock, previously filled with mercury at the mercurial trough, the beaker being rinsed out once or twice with a very small volume of recently-boiled distilled water, and finally with pure and concentrated sulphuric acid, in somewhat greater volume than that of the concentrated solution and rinsings previously introduced into the tube. By a little dexterity it is easy to introduce successively the concentrated liquid, rinsings, and sulphuric acid into the tube by means of the cup and stopcock, without the admission of any trace of air. Should, however, air inadvertently gain admittance, it is easily removed by depressing the tube in the mercury trough, and then momentarily opening the stopcock. If this be done within a minute or two after the introduction of the sulphuric acid, no fear need be entertained of the loss of nitric oxide, as the evolution of this gas does not begin until a minute or so after the violent agitation of the contents of the tube.

"The acid mixture being thus introduced, the lower extremity of the tube is to be firmly closed by the thumb, and the contents violently agitated by a simultaneous vertical and lateral movement, in such a manner that there is always an unbroken column of mercury, at least an inch long, between the acid liquid and the thumb. From the description, this manipulation may appear difficult, but in practice it is extremely simple, the acid liquid never coming in contact with the thumb. In about a minute from the commencement of the agitation a strong pressure begins to be felt against the thumb of the operator, and the mercury spirts out in minute streams, as nitric oxide gas is evolved. The escape of the metal should be gently 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. In from three to five minutes the reaction is completed, and the nitric oxide may then be transferred to a suitable measuring apparatus, where its volume is to be determined over mercury. As half a litre of water is used for the determination, and as nitric oxide occupies exactly double the volume of the nitrogen which it contains, the volume of nitric oxide read off expresses the volume of nitrogen existing as nitrates and nitrites in one litre of water. From the number so obtained the weight of nitrogen in these forms in 100,000 parts of water is easily calculated."

Frankland and Armstrong give two examples to show the degree of accuracy of their process. In one instance 20 milligrms. of nitre were taken, and in the other instances 10 milligrms. The results were :—

	Milligrms. of Nitrogen Calculated.	Found.
No. 1, ...	2·772	2·897
No. 2, ...	1·386	1·424

These determinations exhibit the method as yielding results of fair percentage accuracy, and with an absolute error of $\frac{12}{100}$ milligrms. and $\frac{4}{100}$ milligrms. of nitrogen. In point of accuracy the method is probably as good as is ever actually required for water analysis. We think, however, that it is more trouble than the other method described above. Also, we do not think that it is capable of estimating quantities of nitrogen which fall below $\frac{1}{10}$ milligrm. At any rate, no proof has been offered that such small quantities are estimable by the method.

The circumstance of the binoxide of nitrogen being liberated in contact with some 8 or 10 c. c. of 50 per cent. sulphuric acid, must (even though the liquid be hot) impair the accuracy of the method.

In addition to the processes just given, there are Pugh's method, consisting in the reduction of nitric acid to ammonia by protochloride of tin in sealed tubes at high temperatures, Vernon Harcourt's reduction with iron and zinc, Pelouze's process with proto-salt of iron, and a number of others.

In order to give some idea of the quantities of nitrates and nitrites which occur in different kinds of water, we give a few examples :—

	Grains of Nitric Acid (HNO_3) per Gallon.
London Thames Water Co.,	1·1
London New River Co.,	1·1
London Kent Co. (very pure),	1·3
South Essex Co.,	2·7
Guildford, Surrey (very pure),	1·1
Wells in West of England (very pure),	2·0
Glasgow, from Loch Katrine,	0·1
Manchester, from Derbyshire Hills	0·0
Bala Lake (a dirty water),	0·0

The nitrates and nitrites have been erroneously regarded as measuring the defilement of water. Nitrogenous organic matters decay and are oxidised, and yield more or less nitrates by the oxidation of the nitrogen which they contain. Reflecting on this fact, some chemists have proposed to regard the amount of nitrates in a water (a small correction having been made for the nitrates existing in rain water) as the measure of the sewage which has been discharged into the water and undergone destruction. The recent reports of the Registrar-General on the state of London water refer to these data as showing "*previous sewage contamination.*"

But if nitrates are generated by oxidation of the organic refuse discharged into water, they also find their way into it from the various geological strata traversed by the water. Chalk springs, which contain no organic matter, are often highly charged with nitrates.

Again, on the other hand, the processes of vegetation in rivers and lakes are calculated to withdraw nitrates from the water.

In fine, presence or abundance of nitrates does not show defilement by means of sewage, and deficiency of nitrates does not show absence of defilement. And whilst the high figure for the chalk water of the South Essex Company is no proof of previous sewage contamination of that water, the low figure of Bala Lake does not prove absence of previous sewage contamination of the water of that lake.

We do not look upon the presence of considerable quantities of nitrates in water as any objection to its employment for domestic use.

Iodates, Bromates, and Chlorates.—The existence of traces of *Iodates* in natural waters deserves to be referred to, inasmuch as conflicting reports as to the finding of iodine in certain waters owe their origin to neglect of this possibility. Some experiments recently made in my laboratory have impressed me very strongly with the easy oxidisableness of iodide of potassium; and, in a fully aërated water, I should now be surprised to find iodide of potassium, which I should expect to find oxidised into either iodate or periodate. Bromides and chlorides are not so easily oxidised, but even these salts may undergo oxidation. The way to deal analytically with all cases of this description will be obvious. The water should be acidified, and then boiled with a little sulphurous acid, in order to reduce iodates, &c., into iodides, &c.

CHAPTER X.

GASES AND VAPOURS DISSOLVED BY WATER.

WATER is capable of absorbing, in a greater or less degree, every gas and every vapour which is placed in contact with it.

All water which has been kept in open vessels is necessarily charged with nitrogen and oxygen gases, inasmuch as these gases form the chief constituents of the atmosphere. And if any sample of water be freely shaken up with large volumes of air, it will presently become charged with nitrogen and oxygen in certain well-ascertained proportions, depending on a physical law. A litre of water, freely shaken up with large volumes of air at 15° C. will absorb 17·95 cubic centimetres of air, the composition of which is—

Nitrogen	65·1	vols.
Oxygen, ...	34·9	„
	100·0	„

The composition of the dissolved air is governed by the relative proportions of nitrogen and oxygen gases in the atmosphere, and by the coëfficient of absorption of each gas at the temperature at which the absorption takes place. At 15° C. (according to Bunsen) the absorption coëfficient of nitrogen is 0·0148, and that of oxygen 0·0299, whilst the relative volumes of nitrogen and oxygen in air are—

Nitrogen,	79·0
Oxygen,	21·0
	100·0

The relative proportions of nitrogen and oxygen which water dissolves from the atmosphere at 15° C. are therefore, according to the law, ·0148 × 79 : ·0299 × 21, which gives in percentage—

Nitrogen,	65·1	vols.
Oxygen	34·9	,,
	100·0	,,

If water be taken from rivers and springs, and be bottled up without being freely exposed to the air, it will often be found to exhibit a very different ratio between the dissolved nitrogen and oxygen gases.

Thus, in the autumn of 1859, W. A. Miller found that a litre of Thames' water at Woolwich contained 63·05 c. c. of dissolved gases, the composition of these dissolved gases being:—

CO_2 .	48·3	c. c.
Nitrogen,	14·5	,, ,,
Oxygen,	0·25	,, ,,
	63·05	,, ,,

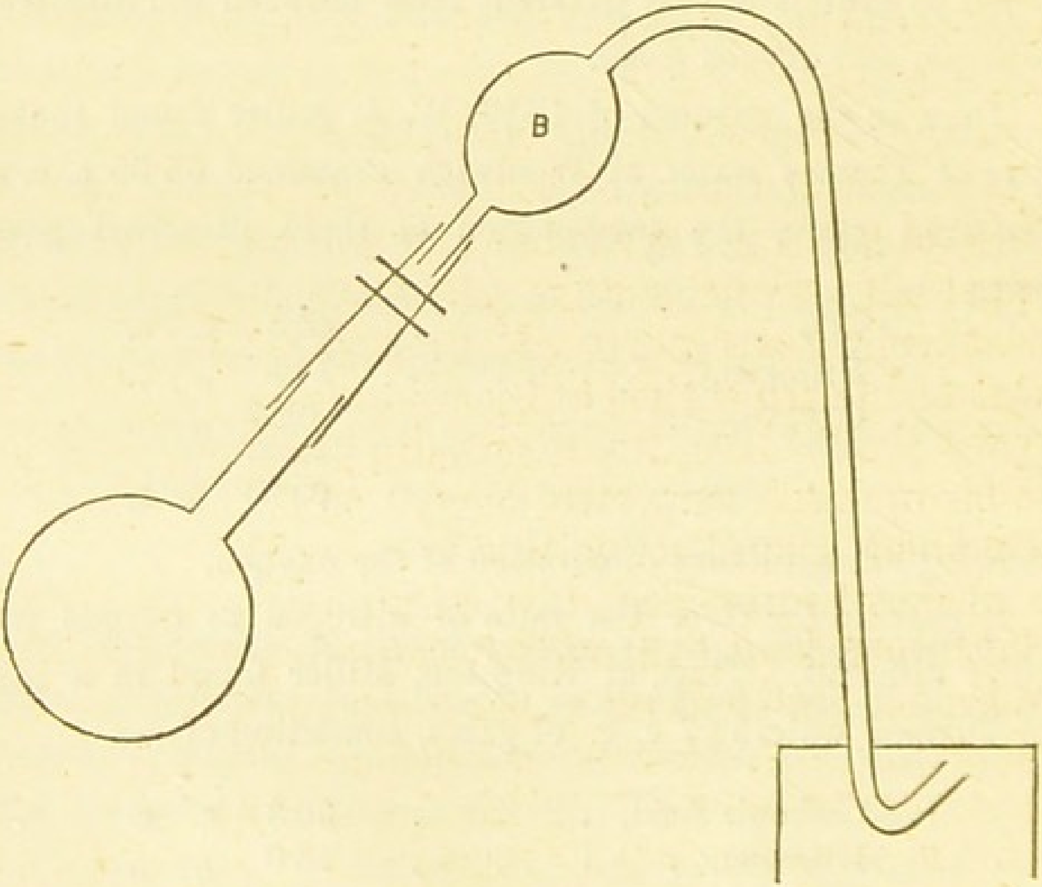
showing extraordinary diminution of the oxygen.

Higher up the river the ratio of nitrogen to oxygen was quite different. Thus, at Kingston, Miller found in a litre of Thames' water52·7 c. c. of gases, consisting of—

Carbonic Acid,	30·3	c. c.
Nitrogen,	15·0	,, ,,
Oxygen,	7·4	,, ,,
	52·7	,, ,,

As will be observed, the ratio of the nitrogen to the oxygen in this water is very nearly that which theory requires in a perfectly aërated water.

Undoubtedly the Thames' water, taken out of the river at Woolwich, owes its deficiency of oxygen to the reducing action of the urea and other matters poured into the river in the form of sewage. And starting from this fact, an attempt has been made to raise thorough aëration as a sort of standard of purity. Very little practical use can, however, be made of the state of aëration, since the purest deep-spring waters are also liable to imperfect aëration. And in this respect the very best and the very worst waters are on a par with one another.



The gases in water are estimated by taking a known volume of water, boiling out the gases, and collecting them over mercury. A flask capable of containing about 500 c. c. of water, and provided with a narrow neck, is filled completely with the sample of water under examination. The neck is surrounded with a stout, tightly-fitting vulcanised indiarubber tube (*vide* fig.) The indiarubber tube is pinched by a clasp, and connects the neck of the flask with an exit tube, on which is blown a bulb B. In the bulb B is placed a little water. The operation is commenced by boiling the water in the bulb B, so as to clear the bulb and exit tube of air. That having been done, the clasp pinching the indiarubber connector is loosened, and the water in the flask is then heated till it boils and has liberated all the gas, which is collected and measured over mercury.

The analysis of the gas is made in an obvious manner. The carbonic acid may be absorbed by potash, the oxygen by pyrogallate of potash, and the nitrogen remains as non-absorbable residue.

Vapours in water.—If a large volume of water be distilled, any traces of foreign liquids which it may happen to contain will distil over with the first small proportion of water. By taking a large volume, and distilling over one-tenth, and then repeating the operation on the distillate, exceedingly minute traces of liquids may be extracted from water. I once, in this way, extracted benzol from a sample of water containing an excessively small proportion of it: and in the course of my research into the action of carbonic oxide on sodium-ethyl (which yields propione) turned both the property which water has of absorbing vapours, and its other property of giving them out on distillation, to good account.

CHAPTER XI.

PURIFICATION OF WATER.

WATERS contaminated with animal and vegetable matters are purified in nature by the gradual oxidation of their organic matter, aided by subsidence, and, in some cases, by filtration through porous strata. The processes of evaporation and condensation which give rise to rain are also natural methods of purification.

Water is purified artificially by the following processes:—

1st, Distillation.
2d, Filtration.
3d, Formation of a precipitate in the water.

Distillation.—This method of purification is seldom resorted to for drinking purposes. It is, however, employed at sea, and we believe that, on the coast of Chili, sea-water is regularly distilled for domestic use. The Abyssinian expedition was for some time supplied by water distilled on board ship, and conveyed to the shore. As coal will distil between seven and nine times its weight of water, the advantage of conveying coal on board ship instead of water is obvious.

Distillation frees water from every solid impurity, but not from ammonia, carbonic acid, and any volatile bases which may be present. By rejecting the first part of the distillate, therefore, which contains most of the impurities, we obtain water free from everything except the traces of organic bases, ammonia, &c., which may be generated from the solid organic matter during the distillation. Perhaps the best method of obtaining pure from common water is to redistil distilled water with a little potash and permanganate of potash, and reject the first portion of the distillate. Such water will be quite free from ammonia, carbonic acid, and organic matter. It will contain air, and perhaps traces of matter dissolved from the condenser. Glass dissolves to a very minute extent, if used as a condenser. Silver is said not to do so; nor has it been observed that a copper condenser communicates any solid matter to distilled water.

Distilled water is flat, and to most people unpalatable; but we know from experience that some people get accustomed to it, and prefer it to all other waters. It, to a great extent, loses its unpleasant flavour if exposed to the air for a few hours.

Filtration.—This is the most common method of purifying water. If a water contains solid particles of a given magnitude, and we pass that water through a wire gauze, the meshes of which are of smaller diameter than the particles, we shall, of course, separate the particles, and unless either the gauze or the particles are elastic, the rate at which the operation is conducted will have no effect on the result. But in filtration, as ordinarily conducted, speed affects the result to a very great extent. In filtering through beds of sand, we may roughly say that the effect of the filtration will be almost inversely as the speed at which the filtration is affected.

If a bottle full of slightly turbid water be laid upon its side, and allowed to stand for twenty-four hours, and then examined, it will be found that the sediment has not only deposited itself on those parts of the glass to which gravitation has carried it, but that, though thickest at the bottom, it has spread itself much higher up, and in many cases is even to be found adhering to the top part of the glass. This circumstance has, doubtless, much to do with filtration.

There is, however, another consideration which will perhaps be most easily explained by an example. When softening water by Clark's process, we obtain a precipitate of finely-divided carbonate of lime. If this operation be conducted in large glass vessels (three to four gallons), we can watch this process of depositing the precipitate. If we do so, we shall observe that the first sign of clearing takes place at the top, a layer of quite clear water making its appearance, and gradually extending downwards. If we ask how this water has become clear, the only answer that can be made is, that the precipitate has moved down to the layer of water beneath it, and thereby rendered that layer thick, for had the precipitate not descended into it, it would, like the top layer, have become clear. In the same way, this second layer, by its depositing, renders that beneath it turbid. If such a vessel of water took six hours to clear, we should expect that by dividing it into six layers by means of five diaphragms, equidistant from each other and from the top and bottom of the water, that the water would clear in one-sixth the time, or one hour. On making the experiment, this is found to be the case. To test this matter more fully, what may be called a "subsidence filter" was constructed. It consisted of a wooden box 12 inches square and 20 inches deep, containing 24 plates of sheet zinc, $\frac{3}{4}$ inch apart. Each plate had 6 holes punched in it, 1 inch in diameter. The holes were near to the side, and had their edges turned up a little; the plates were so arranged that the holes were not opposite each other. A small tap came from just below the lowest plate. Another box like this, but without plates, was also constructed. Both boxes were charged with freshly-softened water, containing chalk suspended in it. The water took about eight hours to clear in the box without the plates, and was quite clear in the one with the plates at the end of twenty-five minutes. This box of plates was next used as a filter, by sending a slow stream of water charged with suspended chalk through it. About 11 gallons an hour of quite clear water could be drawn off. If the speed was increased much beyond this, the water was no longer clear. To render the analogy between this "filter" acting entirely by subsidence and the common sand filter quite plain, the box without the plates had a piece of coarse wire-gauze stretched across it just above the tap. It was then filled with slate chips (the small splinters produced by breaking and chipping slates), and water containing chalk in suspension, as before, filtered through it. The action of this filter was exactly the same as that of the plate filter, except that more water could be passed through it per hour without turbidity. If, however, more than about fifteen gallons per hour was passed through it, the water was slightly turbid, and if the quantity was increased to 20 gallons, it was quite so. Some experiments, substituting very coarse sand for the slate, gave analogous results.

Now, the analogy between the last experiments and the subsidence filter is clear; and we may safely draw the inference that a portion of the work performed by a sand filter is due to subsidence within the filter itself, the particles of sand serving as plates. This is almost proved by the fact, that we can force much of the matter removed by such a filter, through it, by slightly increasing the pressure of water, which would not be the case if the filter acted as a strainer.

The common process of filtration through sand is therefore an operation comprising three distinct methods of purification.

1st, Straining.
2d, Removal of matters by adhesion to the sand.
3d, Subsidence within the interstices of the filter itself.

The first method will vary with the size of the apertures through which the water passes; the second, with the amount of surface in the filtering medium in relation to the amount of water; the third will vary with the speed at which the water travels, and with the size of the aperture through which it passes.

The following are examples of the effect of this kind of filtration on the organic matter in the water:—

Waters taken from the Thames near Hampton Court, where the Water Companies take their Supply.

	Free NH_3.	Albuminoid NH_3.
I. Water taken above the Weir, and some distance above Hampton Court, July 1867,	0·045	0·28
II. Another sample taken below the Weir, July 1867,	0·015	0·23
Sample I. filtered through filter-paper,	0·045	0·21
Sample II. ,, ,,	0·015	0·185
Sample taken above the Weir in September 1868,	0·02	0·22

After the filtration effected by some of the London companies, this water was delivered in London as follows:—

July 1867,	0·01	0·06
September 1868,	0·015	0·07

Some filtering media are said not only to remove organic matter, but to destroy it. They are said to do this by causing the organic matter to combine with the oxygen contained in the water, and thus convert it into innocuous compounds. Foremost amongst the compounds said to possess this property stands animal charcoal. Beyond all doubt, animal charcoal has a wonderful power of freeing water from organic matter, and it does to some extent oxidise the organic matter; but whether to a greater extent than can be accounted for by the oxidation always going on in water exposed to the air, is a question which admits of much doubt. Another proposition which has been advanced by Dr Letheby—viz., that animal charcoal, though it may not oxidise the whole of the organic matter, oxidises that portion of it which is most deleterious to the animal economy—does not admit of argument, as there are no data extant on which to found a conclusion.

The following facts have been experimentally ascertained in regard to this subject:—

Animal charcoal will act in water that contains no free oxygen. This is proved by boiling very finely-divided animal charcoal with water containing protochloride of tin in hydrochloric acid. On transferring this charcoal, still wet, to water that had been well boiled, and protochloride of tin added to it, the animal charcoal removed much of the organic matter. Water treated with protochloride of tin and hydrochloric acid gave ·12 milligramme per litre of organic ammonia; same after treating with animal charcoal, ·05 milligramme.

The animal charcoal which had been used in this operation was diffused through water, and the water distilled with permanganate of potash and potash. The result was, that half the charcoal gave ·16 milligramme organic ammonia; and as 5 litres of water were operated upon, this gave ·064 milligrammes as the produce of the amount of organic matter removed by the animal charcoal. This number shows that here at any rate no destruction of the organic matter took place.

The same experiment was repeated on the same water, but without the deoxidising process. In this case the animal charcoal removed about the same amount of organic matter, but it could not all be recovered from the charcoal. The numbers obtained were:—

From the unaltered water, ...	·13
From the water after treatment with animal charcoal,	·04
From the animal charcoal, ...	·05

The treatment with animal charcoal in all these cases consisted of shaking the water up with the charcoal and allowing it to subside.

Slow filtration through a layer, four inches thick, of animal charcoal in coarse powder removes all organic matter from water, or almost all, but the charcoal fouls to some extent, and after it has been in use with a bad water for some length of time, it lets much of the organic matter pass. If we take some of this charcoal out, and treat it with permanganate of potash and potash, we shall get off ammonia from it in large quantities, proving the presence of organic matter; but if we let it stand for some hours in the air, nearly all the organic matter will be oxidised and disappear. We regret not being able to give more information on this most interesting and important topic, but hope at a future date to be in possession of fuller details.

Other bodies possess in a less degree the same properties as animal charcoal as a filtering agent. A carbide of iron has been much spoken of for filtering purposes. Common wood charcoal has similar properties, though in a much lower degree.

According to Mr Herbert Macleod (*Journal of Chemical Society*, p. 307, for the year 1869), the water of the Grand Junction Co. contained 6·2 c. c. of oxygen per litre; this is about 9 milligrammes. Now, it is obvious that animal charcoal, if used to filter this water, could not oxidise more organic matter than this 9 milligrammes of oxygen would correspond to. In other words, the oxygen in the water is the measure of the utility of the animal charcoal as a destroyer of organic matter, if the filter be used continuously. The advantage of allowing the charcoal to be uncovered with water, and exposed to the air as much as possible when not in use, will therefore be obvious, as it enables the charcoal to charge itself with oxygen afresh, and thereby to free itself from the organic matter which must otherwise have remained in it.

Purification by Precipitation.—The only process requiring detailed remark under this heading is Clark's softening process. Waters to which this method of purification is adapted are such as contain carbonate of lime retained in solution by excess of carbonic acid. The process consists of adding lime to such waters until the excess of carbonic acid is neutralised; when this has taken place both the lime added and that in solution are precipitated as carbonate, a minute quantity remaining in solution, as carbonate of lime is not absolutely insoluble in water. By this process not only is the water softened, but a very large proportion of the organic matter contained in it is removed, and if the water be coloured, the colouring matter is also entirely or in very great part removed.

The following examples will indicate to what extent the organic matter is removed by this process:—

PARTS PER 1,000,000.

		Free NH_3.	Albuminoid NH_3.
I.	Before Clark's process, .	0·01	0·05
	After " " .	0·01	0·02
II.	Before Clark's process, .	0·025	0·22
	After " " .	0·030	0·08
III.	Before Clark's process, .	0·015	0·22
	After " " .	0·020	0·07
IV.	Before Clark's process, .	0·195	0·12
	After " " .	0·15	0·06

It is to be observed, that the organic matter removed can be proved to be present in the chalk precipitated.

The process presents so many advantages, and is so simple, that we are surprised not to see it in general use, and naturally expect to find on investigation that it has some great drawback. This, however, does not appear to be the case. The following objections have been raised to the process :—

1st, That the softened water attacks lead.

2d, That the process is not applicable to waters containing organic matter in large quantity, because the chalk precipitated will not subside.

3d, That as in carrying out the process on a large scale, great volumes of the water must be left at rest for many hours, extra reservoirs would be required, and the expense of waterworks thereby greatly increased.

4th, That the quantity of chalk which would accumulate at the bottom of the reservoirs would require frequent removal; in short, would entail expense.

The first of these objections appears to be founded on error simply. At any rate, it is not valid, as such softened water does not attack lead.

The second objection is to some extent true. Thus Thames water, taken at London Bridge, will not clear when an attempt is made to apply the Clark process to it under many days, and even then the clearance is very incomplete. But Thames water taken at Hampton Court—*i.e.*, at the place where the London water supply is taken—will clear quite well, and in a reasonable time, though perhaps not so quickly as spring water. As no one would think of taking such a water as Thames water at London Bridge as a water supply, this objection does not appear to be of much importance.

The third and fourth objections may be translated by saying, that to soften the water would cost money, a fact that no one is prepared to deny. But when we look at the infinitely more costly schemes which have been proposed for the supply of London, we are compelled to admit that the objection is really frivolous. Moreover, the engineering difficulties might, doubtless, be to a great extent got over by adopting a better system of clearing the water.

One other objection has been raised to the method—viz., that the water pipes "fur," that is, get choked up with a deposit. To this the only reply is, that softened water is now actually being supplied without this inconvenience being felt. Caterham is an instance in point.

The process is one which can be carried out in private houses. We should, perhaps, remark that the point at which enough lime water has been added is found by means of a solution of nitrate of silver. The lime water is added until a sample of the water gives a brown precipitate with the silver solution, instead of a white or yellowish one given by the unaltered hard water. As soon as this is the case, stop the addition of lime water, and add more of the hard water, until the water no longer gives a brown colour with nitrate of silver solution.

The only other methods of purification by precipitation which have been adopted to any extent, are the addition of alum to the water, and the addition of a persalt of iron. In both cases the result is the same—viz., a precipitate is formed which carries down with it a very large proportion of the organic matter, sometimes as much as three-fourths. The Chinese, according to Sherard Osborne, use alum for the purpose of purifying the water of the river Peiho at Tien-tsin.

CHAPTER XII.

URINE AND SEWAGE.

SINCE surface wells, the water from which is often used for domestic purposes, are very liable to contamination with urine and sewage; and since, indeed, the detection of this species of contamination forms an essential part of the duty of the water-analyst, a chapter devoted to those fluids will form a not inappropriate supplement to this book.

The *urine*, as is well known, is an excretion, the composition and quantity of which is subject to great variation, according to the condition of the animal economy.

Thus, among a number of urinary analyses recorded in my own note-book, there is an instance of urine containing 4·52 grammes of solids in 100 c. c., and an instance of urine containing 1·40 grammes of solids in 100 c. c.

The latter specimen of urine had been passed shortly after drinking a quantity of beer, and illustrates a very well-known physiological fact—viz., that after drinking considerable quantities of liquids the urine becomes watery.

In like manner, the quantity of urine produced in the 24 hours is subject to variation, depending to a great extent on the needs of the animal system.

But, although specimens of urine may vary much, and although the quantities of urine excreted under particular circumstances may be very different, still the urine passed by any hundred persons taken at random must be pretty constant both in quality and in quantity.

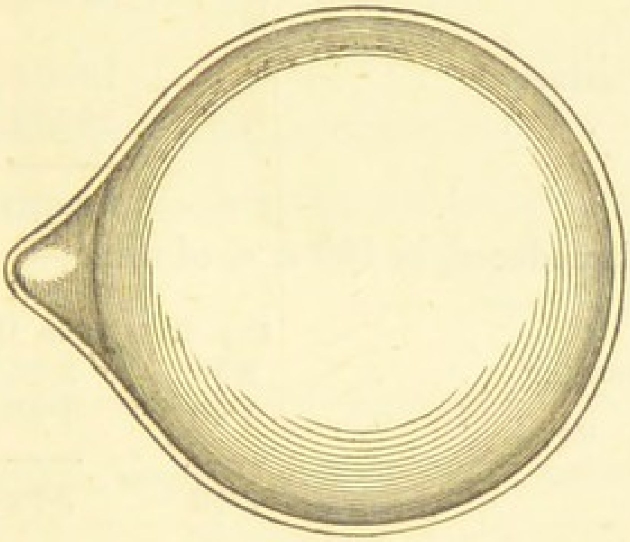
According to Parkes, the average quantity of urine passed by a healthy man in 24 hours is about 1500 cubic centimetres, containing 4·07 grammes of solids in every 100 cubic centimetres. Of these, 4·07 grammes of solids, 2·21 grammes consist of urea. Next in quantity comes the common salt; and thus urine consists chiefly of urea and common salt. In addition to the urea, urine contains some other organic substances in smaller quantities—viz., extractive matter, colouring matter, uric acid, hippuric acid, and creatinine. Besides common salt, there are likewise other mineral ingredients, such as sulphates and phosphates.

A very simple and instructive examination of urine consists in determining the total solids and the "ash." This is done as follows:—

Into a little platinum dish, which has been accurately weighed and placed in the water-bath, 5 c. c. of the sample of urine are accurately measured by means of a suitable pipette. The dish charged with the urine is then exposed to the full heat of the water-bath for two hours, and then taken out of the bath and wiped externally and weighed. The weight of the empty dish having been subtracted from the total weight of dish with urine-residue adherent to it, the difference is the weight of urine-residue yielded by 5 c. c. of urine.

After having weighed the solid residue dry at 100° C., the next step is to ignite carefully, to cool and to weigh again, to get the ash.

These operations resemble closely the taking of solids and ash in milk, (*vide* "Milk-Analysis," by J. A. Wanklyn, published by Trübner and Co.), and require little platinum dishes weighing 12 to 14 grammes, and of the size and shape figured, also a properly-constructed copper bath, with accurately cut holes to receive the platinum dishes, and also an accurate 5 c. c. pipette.



Very constant and accurate results are attainable in these operations, as is exemplified by the following extracts from the laboratory note-book, January 19th, 1872. Urine passed at about 9 A.M., before breakfast, and 12 hours after taking either food or drink.

Exp. I., 5 c. c. taken and evaporated completely in the water-bath.

Dish and urine-residue . . .	12·671	grammes.
Dish	12·483	„
	0·188	

Dish and urine-ash	12·553	grammes.
Dish	12·483	„
	0·070	

Exp. II., 5 c. c. as before.

Dish and urine-residue	12·720	grammes.
Dish	12·534	„
	0·186	

Dish and urine-ash	12·604	grammes.
Dish	12·534	„
	0·070	

From which is deduced, in 100 c. c. of urine—

	Exp. I.	Exp. II.	
Organic matter	2·36	2·32	grammes.
Mineral „	1·40	1·40	„
	3·76	3·72	

A little care is needed in the incineration, so as neither to volatilise chloride of sodium, nor to leave any serious quantity of carbon unburnt. A series of experiments, made in my own laboratory on a number of samples of urine passed by a variety of persons under a variety of circumstances, has led me to the conclusion that in health there is a certain normal ratio between the mineral constituents and the organic constituents of urine, and that during health this ratio is not widely departed from, but that in disease it is widely departed from.

Three examinations of the urine passed by the same healthy person at different dates have given results as follows:—

(Date 1871). In 100 c. c. of urine—

Organic	2·96	grammes.
Mineral	1·56	„

∴ Ratio of mineral to organic = 1 : 1·90.

(Date 1871). In 100 c. c. of urine—

Organic	2·40 grammes.
Mineral	1·46 „

∴ Ratio of mineral to organic = 1 : 1·64.

(Date 1872). In 100 c. c. of urine—

Organic	2·34 grammes.
Mineral	1·40 „

∴ Ratio of mineral to organic = 1 : 1·67.

A different subject, also healthy, yielded urine containing in 100 c. c.—

Organic	2·53 grammes.
Mineral	1.50 „

∴ Ratio of mineral to organic = 1 : 1·69.

Another subject, healthy, yielded urine containing in 100 c. c.—

Organic	2·38 grammes.
Mineral	1·48 „

∴ Ratio of mineral to organic = 1 : 1·61.

Another healthy person, after drinking beer, yielded urine containing in 100 c. c.—

Organic	0·80 grammes.
Mineral	0·60 „

∴ Ratio of mineral to organic = 1 : 1·33.

This last is very instructive as exhibiting no increase in the proportion of organic matter, even when the urine has been rendered too watery by artificial means. In disease, whether merely a transient indigestion, or a permanent organic lesion, the proportion of organic matter in the urine is increased, as exemplified in the following cases:—

No. 1. In 100 c. c. of urine—

Organic matter	3·31 grammes.
Mineral „	1·49 „

∴ Ratio of mineral to organic = 1 : 2·22.

No. 2. In 100 c. c. of urine—

Organic matter . . . . . 5·13 grammes.
Mineral „ . . . . . 1·72 „
∴ Ratio of mineral to organic = 1 : 2·99.

No. 3. In 100 c. c. of urine—

Organic matter . . . . . 2·03 grammes.
Mineral „ . . . . . 0·63 „
∴ Ratio of mineral to organic = 1 : 3·22.

No. 4. In 100 c. c. of urine—

Organic matter . . . . . 2·83 grammes.
Mineral „ . . . . . 1·10 „
∴ Ratio of mineral to organic = 1 : 2·57.

No. 5 (diabetic urine, sugar in abundance). In 100 c. c. of urine—

Organic matter . . . . . 4·42 grammes
Mineral „ . . . . . 1·68 „
∴ Ratio of mineral to organic = 1 : 2·6.

No. 6 (diabetic urine). In 100 c. c. of urine—

Organic matter . . . . . 1·96 grammes.
Mineral „ . . . . . 0·48 „
∴ Ratio of mineral to organic = 1 : 4·08.

These six instances comprise instances of slight derangement of health, Bright's disease and diabetes, and, as will be seen, each exhibits a far higher proportion of organic material than is present in health.

The physician is much in the habit of taking the specific gravity of urine as a guide to the condition of that excretion; but much would be gained if determinations of total solids and fixed solids were substituted for these determinations of specific gravity. The wisdom of such a substitution will be obvious, when it is considered that, although specific gravities and solid contents run tolerably parallel in healthy urine, the parallelism is lost in unhealthy urine, and it is exactly with such urine that the physician has to do.

Urea is the main solid constituent of healthy urine, and the methods of determining it will next be described.

Liebig's Method consists of a titration of the urea in urine, by means of standard nitrate of mercury. The standard mercurial solutions is made by dissolving either mercury, or, still better, peroxide of mercury, in excess of nitric acid, and is graduated by trial with a solution of pure urea of known strength. It is made of such a strength that one cubic centimetre exactly precipitates ten milligrammes of urea.

In using this standard solution for the determination of urea in urine, several circumstances have to be borne in mind. Sulphates and phosphates precipitate the mercurial solution, and have consequently to be got rid of before the employment of the standard solution. Chlorides, on the other hand, retard the production of the white urea-mercury compound, and have likewise to be removed as a preliminary. Albumen also possesses the property of combining with mercurial solutions, and must be removed at once before commencing the testing. Finally, it is only in solutions of a particular strength that the test works correctly, and this introduces a further complication.

The preparation of the urine is accomplished thus:—Any traces of albumen having been removed by a preliminary boiling, two volumes of the sample of urine are mixed with one volume of a baryta solution (which itself consists of two volumes of cold saturated baryta-water, mixed with one volume of cold saturated solution of nitrate of baryta), and filtered. Every 15 c. c. of filtrate contains, therefore, 10 c. c. of the urine. The chlorine in the 15 c. c. is then exactly precipitated by means of silver-solution, and the resulting chloride of silver need not be removed by filtration. To the 15 c. c. of prepared dilute urine, containing 10 c. c. of the original urine, the standard mercury solution may now be added so long as it gives a white precipitate, and until a little of the solution treated with excess of carbonate of soda on a watch-glass begins to give a brownish precipitate of peroxide of mercury. When this point has been reached, the number of cubic centimetres of standard solution must be read off. Every c. c. of mercury-solution corresponds to 0·01 gramme of urea, and, consequently, to 0·1 gramme of urea in 100 c. c. of the sample of urine. If the urine be about of normal strength—*i.e.*, a two per cent. solution of urea, then this titration will work accurately; otherwise, either by suitable dilution with distilled water, or else by a little correction, a result of fair accuracy may be attained.

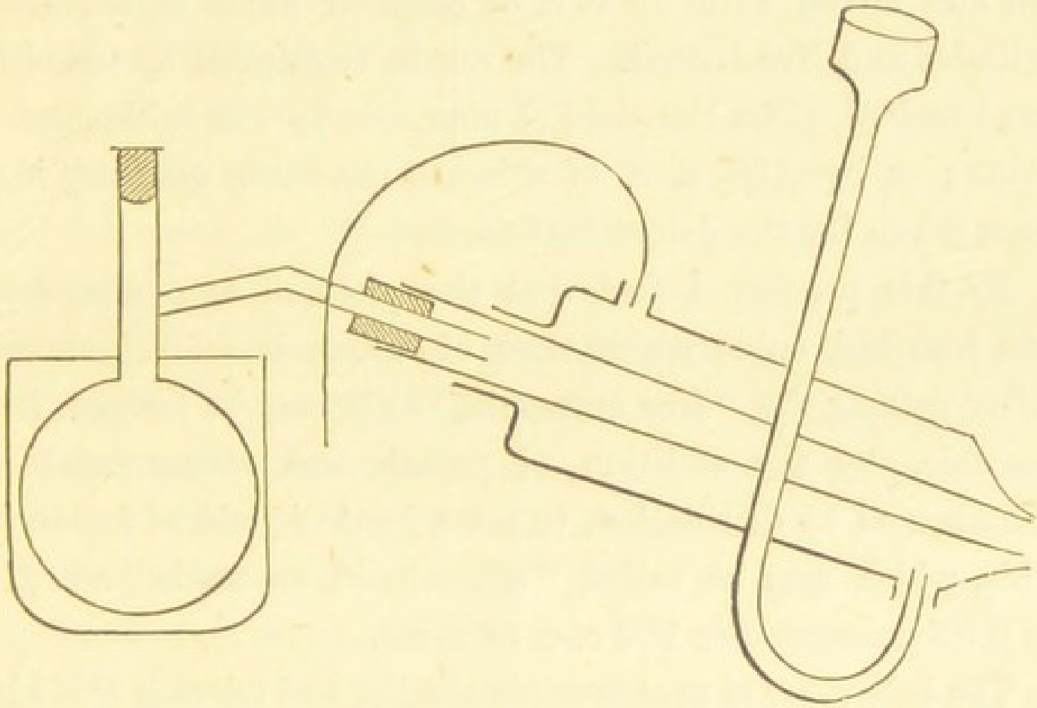
There are also other methods of titrating urea, some of them depending on the reaction of urea on water, whereby it yields carbonic acid and ammonia.

$$CON_2H_4 + H_2O = CO_2 + 2NH_3.$$

I have devised, and am practising, a very convenient titration of urea, the ammonia from which is *Nesslerised*. The method is the following:—

Ten cubic centimetres of a solution of caustic potash, free from all traces of ammonia (strength 10 grammes of solid potash in 100 c. c. of water), are placed in a small flask-retort (capacity about 100 c. c.), which is heated in an oil-bath. Into the potash solution, either one cubic cent. of urine, accurately measured out, or else 10 c. c. of a one-per-cent solution of urine, is dropped, and the whole heated to 150° C. in the oil, or spermaceti bath, until the potash inside the flask-retort has nearly dried up. During this operation the flask-retort is neatly connected with a small Liebig's condenser, *vide* fig.

When the contents of the flask-retort appear nearly dry—*i.e.*, when a temperature of 150° C. has been maintained for a short period in the interior of the flask, the temperature should be lowered. This is done by getting the flask out of the hot oil or spermaceti, and either the oil-bath may be lowered down away from the flask, or else the flask, which is to be maintained in firm connection with the Liebig's condenser, may be raised out of the oil.



If the Liebig's condenser be held by a proper kind of clamp, made of metal lined with cork, and very firm and convenient, this raising up of the apparatus will be found to be quite easy.

In a minute or two the flask-retort will have become cool enough to admit of the introduction of 20 c. c. of distilled water free from ammonia; and that having been done, the oil-bath is again applied to the retort, and the distillation proceeded with. This is continued almost to dryness. The resulting distillate is to be diluted with water until exactly equal to 50 c. c., and having been well stirred up, one-tenth of it (*i.e.*, 5 c. c.), or one hundredth (*i.e.*, 1 c. c.), is to be measured out and mixed with 50 c. c. of distilled water in a Nessler cylinder and Nesslerised. The result, multiplied by ten or by one hundred, gives the yield of ammonia by one cubic cent. of urine; or by $\frac{100}{1000}$ c. c. of urine, if the latter quantity have been taken for the determination.

By this process I find that the yield of ammonia, from one hundred cubic centimetres of utine, is 0·90 grammes. After getting the "free ammonia," as it may be termed, it is possible, by the addition of potash and permanganate of potash, and by distillation, to get a further yield of ammonia. This, which may be called "albuminoid ammonia," amounts to 0·05 grammes per 100 c. c. of urine.

The behaviour of urea towards alkalies and towards oxidising agents in alkaline solutions is very remarkable and characteristic. Urea, when *quite* pure, may be boiled for a long time with alkalies without evolving a trace of ammonia; and even when impure, though slowly decomposed, yet the decomposition is exceedingly slow. But at temperature some way above 100° C., the decomposition is very rapid and complete.

In presence of permanganate and excess of potash, urea is doubtless decomposed, but it yields no ammonia, which is a very extraordinary and noteworthy fact. The property of yielding a torrent of ammonia when heated to 150° C. with caustic alkali, and no ammonia at all when boiled with alkaline permanganate solution, is, I believe, quite characteristic of urea. I have, in the course of a very wide experience, never come across another substance which resembles it in this respect.

The further analysis of urine need not be entered into in this place.

Sewage.—In London each inhabitant is supplied with, on an average, at least, 30 gallons of water daily. This 30 gallons of water per head, mixed with the urine and excrement, and with soap, &c., constitutes the sewage of London.

Taking the quantity of urine voided daily as 3 lbs. per head, and the water as 30 gallons (or 300 lbs.), the sewage will contain one per cent. of urine. In becoming diluted and mixed with other matters so as to form sewage, urine appears to undergo a very rapid fermentation, and yields carbonate of ammonia, so that sewage is sometimes found to be almost devoid of urea, but charged with ammonia.

Taking sewage as a solution, containing one per cent. of urine, and urine as yielding one per cent. of ammonia, sewage ought to contain 0·01 per cent of ammonia, or 100 parts of ammonia per million. In urine there is likewise ·05 per cent. of "albuminoid ammonia;" therefore, in sewage there should be 5·00 milligrammes per litre of albuminoid ammonia.

Most samples of sewage appear, however, to fall short of these quantities, and it is by no means impossible that the ureal fermentation is attended with loss of nitrogen in the form of nitrogen gas.

APPENDIX.

THE original memoirs, describing our researches into the action of oxidising agents on a great variety of organic substances in strongly alkaline solution, are reprinted from the *Journal of the Chemical Society*. The chapter entitled "Hardness" in former editions of this book, is likewise reprinted under the title "Dr Clark's Soap Test" in this appendix.

Experiments illustrative of the constancy of the ratio between the yield of albuminoid ammonia, and the strength of the albuminous fluid operated upon (*Vide Journal of the Chemical Society* for the year 1867, page 593):—

	Moist white of egg. Milligrammes employed.	Milligrammes of NH_3.	
		Found.	Theory.
I.	17·69	0·210	0·214
II.	17·58	0·213	0·2127
III.	41·80	0·505	0·5058
IV.	27·87	0·350	0·337
V.	12·20	0·145	0·1476
VI.	7·47	0·095	0·0904
VII.	23·065	0·275	0·279

ON THE ACTION OF OXIDISING AGENTS ON ORGANIC COMPOUNDS IN PRESENCE OF EXCESS OF ALKALI.

By J. Alfred Wanklyn, Professor of Chemistry in the London Institution, and E. Theophron Chapman.

Part I. *Ammonia evolved by Alkaline Permanganate acting on Organic Nitrogenous Compounds.*

It has been observed that albumen evolves ammonia when submitted to the action of permanganate of potash in strongly alkaline solutions.* Furthermore, that this ammonia is perfectly constant in quantity, being strictly proportional to the amount of albumen employed, and that it is not the whole, but only a fraction, of the total ammonia which the total nitrogen of the albumen is capable of furnishing.†

On extending this inquiry to organic nitrogenous substances in general, we find the action of strongly alkaline permanganate to be perfectly definite, as will be apparent from the results to be given further on.

We shall confine ourselves, in this paper, to a consideration of the ammonia evolved, and in subsequent papers, in continuation of the subject, hope to render account of the residual nitrogen (when there is any) and of the other complementary products of the oxidation.

We will first describe the mode of conducting the experiments.

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* Wanklyn, Chapman, and Smith, *Journal of the Chem. Soc.* (1867), vol. v. [Ser. 2], 445.

† *Ibid.* Wanklyn (1867), vol. v. [Ser. 2], 591.

The ammonia evolved during the reaction was (as in the papers just referred to) measured by means of the Nessler test, and inasmuch as this test is used with very small quantities of ammonia, it was convenient to operate on very small quantities of organic matter.

In order to measure these small quantities with the necessary degree of precision, the following plan was usually adopted :—

100 milligrammes of the substance to be oxidised were weighed out and dissolved in 100 c. c. of water, thus giving a solution containing one milligramme in a cubic centimetre of the solution. By measuring this solution in an accurate burette divided into tenths of a cub. cent., or by weighing out, there was obtained the requisite quantity of the organic substance measured with the requisite degree of accuracy.

The oxidation was usually effected as follows :—Half a litre of freshly-distilled water was put into a retort, then 50 c. c. of a solution of potash (equal to 10 grammes of solid potash) were added.

Then about 100 c. c. were distilled over, and usually found to be ammoniacal. This having been done, the further distillate was generally found to be ammonia-free.

Next some permanganate of potash (from 0·1 to 0·5 grm.) was added, also a few fragments of freshly-ignited tobacco-pipe (Mr Duppa's device to avoid bumping and violent boiling).

Then the weighed, or measured liquid, containing the substance to be oxidised, was put into the retort, and the distillation proceeded with.

The distillation was continued until the evolution of ammonia ceased or became very trifling.

Blank trials having been made with the distilled water and reagents, the following substances were investigated :—

I. *Asparagine*, $C_4H_8N_2O_3 + H_2O$.—The sample of asparagine was obtained from Messrs Hopkin and Williams, and was in beautiful crystals. It was dissolved in water.

Milligrammes.
Substance taken = 3·65
NH_3 obtained = 0·80
NH_3 per cent. = 21·92.

II. *Piperine*, $C_{17}H_{19}NO_3$.—From Messrs Hopkin and Williams, was well crystallised. It was dissolved in glacial acetic acid.

Milligrammes.
Substance taken = 4·25
NH_3 obtained = 0·23
NH_3 per cent. = 5·41.

III. *Chloride of Diamylamine*, $(C_5H_{11})_2H_2NCl$.—Prepared in the laboratory of the London Institution, analysed, and found to be pure.

Milligrammes.
Substance taken = 3·91
NH_3 obtained = 0·31
NH_3 per cent. = 7·93.

The volatility of the substance rendered it difficult to get complete action, which accounts for the NH_3 being too low.

Diamylamine gives a white precipitate with the Nessler-test.

IV. *Amylamine*, $C_5H_{13}N$.—Prepared in the laboratory of the London Institution, by the action of iodide of amyl on ammonia. Had a perfectly constant boiling-point. Its chloro-platinate and chloride were analysed and found to be pure. It was very carefully freed from ammonia, and give with Nessler-test a pure white (not a brownish) precipitate.

		I. Milligrms.	II. Milligrms.
Substance taken,	=	2·70	1·10
NH_3 obtained,	=	0·59	0·24

NH_3 per cent. = 21·8. NH_3 per cent. = 21·8.

V. *Diphenyl-tartramide,* $C_{16}H_{16}N_2O_4$.—Presented to us by Mr Perkin.

		Milligrms.	Milligrms.
Substance taken	=	7·2	19·4
NH_3 obtained	=	0·70	1·98
NH_3 per cent.	=	9·72	10·21.

The foregoing examples are instances of total conversion of the nitrogen of the substance into ammonia, as the following comparison shows :—

	Theory.	Found.
I. Asparagine, . .	22·66	21·92
II. Piperine, . . .	5·96	5·41
III. Diamylamine Chloride,	8·79	7·93
IV. Amylamine, . .	19·54	21·8
V. Diphenyl-tartramide, .	11·32	10·21

The first column of figures contains the calculated quantity of ammonia which 100 parts of the substance could give if all its nitrogen passed into ammonia. The second column gives the ammonia obtained from 100 parts of substance.

Piperidine, hippuric acid, and narcotine, also give up the total nitrogen in the form of ammonia, on being boiled with strongly alkaline permanganate.

VI. *Morphine,* $C_{17}H_{19}NO_3$.—Obtained from Greville Williams, dried at 100° C.

		Milligrammes.
Substance taken	=	20·
NH_3 obtained	=	0·56
NH_3 per cent.	=	2·8.

VII. *Codeine*, $C_{18}H_{21}NO_3H_2O$.—Splendid crystals from Macfarlane, of Edinburgh.

Milligrammes.
Substance taken = 6·5
NH_3 obtained = 0·195
NH_3 per cent. = 3·00.

VIII. *Papaverine*, $C_{20}H_{21}NO_4$.—From Macfarlane of Edinburgh. In good crystals.

Milligrammes.
Substance taken = 10·0
NH_3 obtained = 0·22
NH_3 per cent. = 2·2

This substance yields up the ammonia with extreme difficulty.

IX. *Strychnine*, $C_{21}H_{22}N_2O_2$.—From Messrs Hopkin and Williams. In very good crystals, carefully dried.

Milligrammes.
Substance taken = 5·5
NH_3 obtained = 0·30
NH_3 per cent. = 5·45.

X. *Iodide of Methyl-strychnine*, $C_{21}H_{22}(CH_3)N_2O_2I$.—From Dr Crum Brown. Good crystals.

Milligrammes.
Substance taken = 7·2
NH_3 obtained = 0·24
NH_3 per cent. = 3·33.

XI. *Brucine*, $C_{23}H_{26}N_2O_4$.—From Messrs Hopkin and Williams.

Milligrammes.
Substance taken = 10·
NH_3 obtained = 0·46
NH_3 per cent = 4·6.

XII. *Sulphate of Quinine*, $(C_{20}H_{24}N_2O_2)_2H_2SO_4$.—From Messrs Hopkin and Williams. It was carefully dried.

Milligrammes.
Substance taken = 10·00
NH_3 obtained = 0·45
NH_3 per cent. = 4·5.

XIII. *Sulphate of Cinchonine*, $(C_{20}H_{24}N_2O)_2H_2SO_4$.—From Messrs Bullock. It was recrystallised in the laboratory of the London Institution, and dried at 100° C.

		Milligrms.	Milligrms.
Substance taken	=	10·00	5·00
NH_3 obtained	=	0·57	0·27

NH_3 per cent. = 5·7. NH_3 per cent. = 5·4.

These numbers (as will be apparent from the tabular statement a little further on) are somewhat in excess of the theoretical quantity for sulphate of cinchonine.

As is abundantly evident, however, from the researches which have been published on cinchonine, the formula of this substance is by no means well established. The formula just given yields 4·76 for half of the ammonia. Other formulæ which have been proposed give close on 5·00 for half of the ammonia.

XIV. *Nicotine*, $C_{10}H_{14}N_2$.—From Messrs Hopkin and Williams.

Milligrammes.
Substance taken = 1·99
NH_3 obtained = 0·215
NH_3 per cent. = 10·80.

Nicotine has no action on the Nessler-test.

XV. *Naphthylamine*, $C_{10}H_9N$.—Prepared by ourselves from nitronaphthaline. The hydrochlorate was analysed and found to be pure.

	Milligrms.	Milligrms.
Substance taken =	12·175	4·26
NH_3 obtained =	0·81	0·29

NH_3 per cent. = 6·65. NH_3 per cent. = 6·81.

Naphthylamine has no action on the Nessler-test.

XVI. *Toluidine*, C_7H_9N.—A well-crystallised specimen, obtained from the Continent.

	Milligrms.	Milligrms.
Substance taken =	4·08	2·65
NH_3 obtained =	0·36	0·22

NH_3 per cent. = 8·83. NH_3 per cent. = 8·30.

Toluidine has no action on the Nessler-test.

XVII. *Acetate of Rosaniline*, $C_{20}H_{19}N_3C_2H_4O_2$.—Dried at 115° C.

	Milligrms.	Milligrms.
Substance taken =	3·925	4·626
NH_3 obtained =	0·25	0·30

NH_3 per cent. = 6·37. NH_3 per cent. = 6·49.

In the following table, under theory, there are numbers calculated on the principle that 100 parts of the substance should give up half its nitrogen in the form of ammonia :—

		Theory NH_3.	Found NH_3.
VI.	Morphine,	2·98	2·80
VII.	Codeine,	2·67	3·00
VIII.	Papaverine,	2·50	2·20
IX.	Strychnine,	5·09	5·45
X.	Iodide of methyl-strychnine,	3·57	3·33
XI.	Brucine,	4·32	4·60
XII.	Sulphate of quinine,	4.56	4·50
XIII.	Sulphate of cinchonine,	4·76	5·7 5·4
XIV.	Nicotine,	10·49	10·80
XV.	Naphthylamine,	5·95	6·65 6·81

	Theory NH_3.	Found NH_3.
XVI. Toluidine, ...	7·95	8·83 8·30
XVII. Acetate of Rosaniline, . . .	7·06	6·37 6·49

An instance of the evolution of one-third of the nitrogen in the form of ammonia, is afforded by creatine $C_4H_9N_3O_2$. The specimen of creatine taken for the experiments was kindly given to us by Mr Greville Williams. It was dried and analysed, giving a correct result.

The mean of three accordant determinations of the ammonia evolved on boiling 100 parts with alkaline permanganate, is 12·6. The theoretical quantity, on the principle of evolution of one-third of the nitrogen as ammonia, is 12·98.

This result becomes intelligible when it is remembered that two-thirds of the nitrogen in creatine are present in the form of *urea*, and that the nitrogen of urea is evolved by alkaline permanganate, either as nitrogen gas or as nitric acid. Sarcosine, the form in which the residual third of the nitrogen is contained, will, we believe, be found to give up all its nitrogen as ammonia.

In theine we have found a substance which gives up one-fourth of the nitrogen as ammonia.

Found, NH_3 from 100 parts
= 8·54
Theory = 8·76 (¼ of the nitrogen).

The molecule of theine contains four atoms of nitrogen.

Theine, $C_8H_{10}N_4O_2$.

Uric acid also gives up a comparatively small fraction of its nitrogen in the form of ammonia.

Apparently, 100 parts of uric acid yield about 7 parts of NH_3; we shall, however, experiment further on this substance. We subjoin determinations made on substances of which the molecular weight is unknown.

100 parts of gelatin have given 12·7 parts of NH_3.

*100 parts of casein gave 7·6 parts of NH_3.

100 parts of dry albumin give about 10 parts of NH_3.

We mention, lastly, an experiment on a substance containing the whole of its nitrogen in the nitro-form, viz., picric acid, $C_6H_2(NO_2)_3HO$. It gave no ammonia on distillation with alkaline permanganate, but yielded nitric acid, as was proved by subsequently getting abundance of ammonia on reducing the alkaline liquid by means of aluminium.

Before considering the general conclusions to be drawn from the experimental data contained in this paper, we think it useful to give a special description of the method of research which has been followed, and a discussion of some points connected with it.

The extreme minuteness of the quantities of substance subjected to quantitative determination is one of the most striking features of this investigation, and of those investigations more or less connected with it which have been published within the last year. On looking back, it will be seen that the quantity of substance taken for analysis varies from one to twenty milligrammes, being generally much nearer the former than the latter limit. In short, it may be said, without greatly exaggerating, that we have substituted milligrammes for the grammes which are ordinarily experimented on. As will have been observed, we have, accordingly, all through-

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* Of very doubtful purity.

out the paper given the weights in milligrammes instead of grammes.

The first point to be considered is the mode of effecting the requisite division of the substance. In one instance wherein the larger quantities were taken, as, for example, in the instance of diphenyltartramide, the substance was weighed on a bit of platinum foil, and employed in the solid state. In every other case, the substance was employed in solution. As was described at the beginning of the paper, the usual way of proceeding was to weigh out 100 milligrms. of substance and dissolve it in 100 cub. cent. of water, or very dilute acid or alkali, according to circumstances. The dilute solution might then, if necessary, be weighed out accurately to a milligramme, and so the substance experimented on would be capable of being divided accurately to $\frac{1}{1000}$ of a milligramme.

If ordinary care be taken, no fear need be entertained that the water used for making these dilute solutions will contain sufficient ammonia or other nitrogenous substance to vitiate the experiments. There is no great difficulty in preparing distilled water of such purity as not to give so much as $\frac{1}{100}$ milligrm. of ammonia per litre. But, for making these solutions, it is not requisite to use anything better than ordinarily well-distilled water, which, made from the London water, seldom contains more than $\frac{10}{100}$ or $\frac{15}{100}$ milligramme of ammonia per litre.

Thus taking water of this quality, we will suppose 10 cub. cent. to be employed. There would be then 10 milligrms. of substance employed, and an error of $\frac{1}{1000}$ of a milligrm. of ammonia introduced by reason of impurity of the water. In short, a little consideration will easily show that there is no reason for apprehending the vitiation of results in consequence of error affecting the division of the substance taken for experiment.

By a proper system of washing the apparatus, carefully cleaning out the Liebig's condenser by distilling water through it immediately before using it for an experiment on the estimation of these minute quantities of ammonia, and by carefully testing all reagents employed, it is quite easy to avoid the introduction of extraneous ammonia, and to obtain perfectly regular results.

It may be well to refer specially to the precautions to be taken in making a delicate testing of the purity of distilled water. The utmost freedom from all traces of ammonia is essential, for instance, in the case of the half-litre of water which is destined to receive the small quantity of substance, the ammonia evolved by the oxidation of which is to be estimated. In cases like this, it is not enough that 100 cub. cent. of the water should give no coloration with the Nessler-reagent, but 100 cub. cent. of the first distillate given by one litre of the water should give no reaction with the Nessler-reagent. Precise and detailed directions for the preparation and use of the Nessler-test will be found in the "Laboratory," vol. i., p. 267. To these directions we may add that we find it convenient to have our standard solution of ammonia of such a strength that one cub. cent. contains $\frac{1}{100}$ milligramme of ammonia, and that if, as sometimes happens, the Nessler-reagent should prove wanting in sensitiveness, the addition of a little solution of bichloride of mercury will render it sensitive.

Connected with the indications of the Nessler-test we have observed a point of some interest, which deserves to have attention directed to it. We have not met with any base except ammonia which gives the peculiar brownish coloration with the Nessler-reagent. Amylamine, diamylamine, and piperidine in very dilute solutions, give white opalescence or precipitate when treated with the Nessler-test; naphthylamine, toluidine, and nicotine, under these circumstances, occasion no reaction of any kind. (Although, however, these volatile bases cause no coloration, yet their presence more or less affects the tint which ammonia gives with the Nessler-test, and they thus, to some extent, interfere with the sharpness of the estimation of ammonia.)

There is, therefore, every reason for believing that the production of the brownish tint with the Nessler-test is quite characteristic of ammonia. The degree of precision attainable in reading the indications of the Nessler-test is much greater than would be imagined at first sight. The $\frac{5}{1000}$ of a milligrm. of NH_3 in 100 c. c. of liquid is a quantity very easily seen. The difference between $\frac{10}{100}$ and $\frac{20}{100}$ of a milligramme of NH_3 will, we think, be visible to most people. With practice a higher degree of precision is attainable. When, instead of using 100 c. c. of water for the Nessler-test, a smaller bulk is taken, the indications become more delicate. So small a quantity as $\frac{1}{1000}$ of a milligramme of ammonia may be seen in a small bulk of liquid.

In short, the Nessler-determination of ammonia is susceptible of the most wonderful delicacy.

On referring to the results given by different substances, as described in this paper, it will be seen that, putting nitro-compounds on one side, organic nitrogenous substances in general evolve ammonia on being heated to 100° C. with strongly alkaline solution of permanganates. This reaction is very general, as an inspection of the very varied list of substances contained in this paper is sufficient to show. The compound ammonias of all kinds, the amides of the acids, such substances as piperine, hippuric acid, creatine, the natural alkaloids, albumin, gelatin, and uric acid, evolve ammonia when treated in this way. Even so tough a substance as picoline, which, as is well known, is one of the most stubborn of organic compounds, yields ammonia when subjected to this treatment. Except in the instance of nitro-compounds, urea, and ferrocyanide of potassium, we have not met with any unequivocal instance of failure of an organic nitrogenous substance to evolve ammonia on being heated to 100° C., with a strongly alkaline solution of permanganate.

In the matter of the nitro-compounds, there is, be it observed, some degree of resemblance between our process and the Will and Varrentrapp process.

This difference, however, is to be noted. The Will and Varrentrapp process gives irregular results when applied to nitro-compounds, part of the nitrogen of such compounds forming ammonia, and part not forming ammonia. Our process, on the other hand, does not convert *any* nitro-nitrogen into ammonia, but into nitric acid instead, being perfectly regular in its indications with nitro-compounds. It will be understood that, having converted the nitro-nitrogen into nitric acid, we may subsequently reduce that acid to ammonia by means of aluminium, as exemplified in the instance of picric acid above described.

On inquiring into the other peculiarities of structure which prevent alkaline permanganate evolving nitrogen of a given organic compound in the form of ammonia, our attention is arrested by the example of urea, which evolves none of its nitrogen as ammonia when so treated. The reason of this peculiarity is not far to seek, being at once visible in the formula. Urea is in a sense a perfectly oxidised substance, requiring the elements of water to transform it into carbonic acid and ammonia, and if simply oxidised, would exhibit a deficiency of hydrogen—there would be CO_2, and only 4H along with the N_2.

As we have seen, compounds formed by the juxtaposition of urea with another substance, with elimination of water (as for instance creatine, which, as is well known, is so formed from urea and sarcosine) share this property with urea, and do not give up their ureic nitrogen in the form of ammonia. Possibly uric acid furnishes so small a proportion of its nitrogen as ammonia, owing to the existence of nitrogen in the ureic state; and possibly the non-evolution of part of the nitrogen of albumin is due to the same cause.

On turning to the early part of the paper, it will be seen that whilst amylamine, diamylamine, and piperidine, substances all derived from homologues of marsh gas, undergo total conversion into ammonia, the bases toluidine, napthylamine, and nicotine, substances which are derived from hydrocarbons lower than the homologues of marsh gas, undergo only a half-conversion into ammonia. This circumstance points to the conclusion that derivation from a so-called saturated hydrocarbon implies easy conversion of the nitrogen into ammonia, whilst derivation from an unsaturated hydrocarbon interposes difficulties in the way of conversion into ammonia.

The conversion into ammonia of only half the nitrogen of so many of the natural alkaloids is an interesting fact. Some light is thrown upon it by the example of narcotine, which although it gives up all its nitrogen as ammonia, gives it up only slowly, and by dint of putting back the distillate; it doubtless also yields parts of its nitrogen as methylamine in the first instance. A careful examination of strychnine has disclosed a somewhat similar state of matters in the case of that alkaloid. Apparently the missing half of the nitrogen in strychnine passes provisionally into the state of some volatile alkaloid. As we said at the commencement, we reserve the treatment of the residual nitrogen for a future occasion.

NEW TESTS FOR SOME ORGANIC FLUIDS.

By J. Alfred Wanklyn, Corresponding Member of the Royal Bavarian Academy of Sciences.

In the course of the investigations connected with the establishment of the ammonia process of water-analysis, it soon became apparent that Chapman, Smith, and myself had in our possession a new instrument of chemical research, and in using this instrument I have, I believe, come across some very characteristic properties of the commoner animal fluids. When an animal fluid is mixed with excess of potash, evaporated down in contact with the alkali, and then maintained at a temperature of about 150° C. for some time, it evolves a certain fixed proportion of ammonia. This having been accomplished, a further quantity of ammonia may be got by boiling the residue with alkaline solution of permanganate of potash. Now, for certain animal fluids, the quantity of ammonia yielded by a given weight or volume of the animal fluid is characteristic; and the relative quantities of ammonia obtained by potash and by permanganate of potash are likewise characteristic. Thus are provided two new criteria of these animal fluids, which may become of some importance in practical biology, and especially in some of those inquiries which the medical jurist is called upon to conduct.

My investigations on this subject are far from complete, but still they are sufficiently advanced to enable some idea to be formed of the scope and possibilities of such work.

Of all the animal fluids, I know of only one which yields a large proportion of ammonia to caustic potash, and that fluid is urine. On the other hand, urine is distinguished by the smallness of the yield of ammonia to permanganate of potash.

Milk yields about half as much ammonia to potash as to permanganate of potash.

Blood yields about one-fifth as much ammonia to potash as to permanganate of potash.

White of egg, moist, just as it occurs naturally, gives about one-fourth as much ammonia to potash as to the permanganate.

Gelatin, strange to say, gives no ammonia (or only the least trace) to potash, and a good quantity to permanganate.

It is, moreover, a fact pregnant with interest, that if the preliminary heating to 150° C. with caustic potash be omitted, and if the boiling with permanganate be at once proceeded with, only that quantity of ammonia is obtained which would have been yielded to permanganate of potash if the entire process had been gone through. I have, in another place, insisted upon this being interpreted to mean that casein and albumin are chemical compounds into which urea enters as a constituent part, and that gelatin contains no urea.

I will next give the experimental numbers.

100 cubic centimetres give—

Name of Fluid.	Ammonia by Potash at 150° C.	Ammonia by Permanganate of Potash.
Urine (human)	0·90 gramme.	0·05 gramme.
Milk of cow	0·13 ,,	0·28 ,,
Blood of sheep	0·46 ,,	2·20 ,,
Liquid white of egg (hen) . .	0·32 ,,	1·30 ,,
Dry solid gelatin (100 grams)	0· gramme.	10· grammes.

These numbers must be looked upon as fair approximations, and may require a little rectification in the progress of the inquiry.

With regard to the possible applications of this work to the elucidation of questions before the medical jurist, I would suggest, just as an instance, the possibility of distinguishing between a spot of milk and a spot of white of egg on a cambric handkerchief, for these investigations are appropriately carried out on minute quantities.

In conclusion, it may, perhaps, be useful to state, that in the above experiments, 5 c.c. of the animal fluid were mixed with water in a 500 c.c. flask, and diluted up to the 500 c.c. mark, thereby forming a dilute solution, whereof 1 c.c. contained $\frac{1}{100}$ c. c. of the animal fluid; that 5 or 10 c. c. of this dilute liquid were usually taken for one experiment, and that a delicate little retort fitted to a delicate little Liebig's condenser was employed. The retort was heated in an oil-bath. The ammonia was measured by the Nessler-test.

DR CLARK'S SOAP-TEST.

One of the most important domestic uses of water is to wash with, and one of the most striking differences between different kinds of natural water is the behaviour of it towards soap. Some water destroys much soap before a lather is formed; such water is said to be hard. Other kinds of water admit the formation of a lather almost instantly, and are said to be soft.

The destruction of soap is due to the formation of insoluble salts, by reaction between the lime and magnesia of the water and the soap. Not until the lime and magnesia salts present in the water have exhausted themselves upon the soap (forming insoluble lime or magnesia salts of the fatty acids of soap), will there be formation of lather. In measuring the hardness of water, there are two obvious ways of constructing the scale of hardness. We may measure the amounts of soap destroyed by a volume of different kinds of water; or, bearing in mind the cause of hardness in a water, we might measure the amount of fixed matter in a volume of different kinds of water. On the one plan, the degree of hardness is the quantity of soap destroyed—so much soap destroyed, so many degrees of hardness. On the other plan, the degree of hardness is the quantity of carbonate of lime (or its equivalent of other salts) in the water. Both methods of registering hardness are intelligible, but the former is direct; and regard being had to the fact that it is the actual consumption of soap that we want practically to know, it is better to regard "degrees of hard ness" as quantities of soap destroyed, and not as quantities of carbonate of lime which do damage by destroying soap.

We transcribe the following account of the soap test from Dr H. M. Noad's valuable little book on "Quantitative Analysis," p. 576:—

"(*a*) We are indebted to Dr Clark for a very simple method of determining the *degree* of hardness of a water. It consists in ascertaining the quantity of a standard solution of soap in spirit required to produce a permanent lather with a given quantity of the water under examination; the result being expressed in degrees of hardness, each of which corresponds to one grain of carbonate of lime in a gallon (=70,000 grains of distilled water) of the water. From the specification of his patent (enrolled 8th September 1841), we gather the following particulars:—

"(*b*) *Preparation of the Soap Test.*—Sixteen grains of pure Iceland spar (carbonate of lime) are dissolved (taking care to avoid loss) in pure hydrochloric acid; the solution is evaporated to dryness in an air-bath, the residue is again redissolved in water, and again evaporated; and these operations are repeated until the solution gives to test-paper neither an acid nor an alkaline reaction. The solution is made up by additional distilled water to the bulk of precisely one gallon. It is then called the 'standard solution of 16 degrees of hardness.'* Good London curd soap is dissolved in proof spirit, in the proportion of one ounce of avoirdupois for every gallon of spirit; and the solution is filtered into a well-stoppered phial, capable of holding 2000 grains of distilled water; 100 test measures, each measure equal to 10 water-grain measures of the standard solution of 16 degrees of hardness, are introduced. Into the water in this phial the soap solution is gradually

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* The "standard solution of 16 degrees of hardness" may be obtained much more simply by dissolving in a gallon of water a quantity of selenite equivalent to 16 grains of carbonate of lime. As the formula of selenite is $Ca_2SO_4\ 2H_2O=172$, and that of carbonate of lime $Ca_2\ CO_3=100$, the following proportion gives us the quantity of selenite required:—$100 : 172 : : 16 : x$; $x=27{\cdot}52$. The selenite should be reduced to fine powder before it is weighed. It dissolves without difficulty. I do not know who first proposed this method.—E. T. C.

poured from a graduated burette ; the mixture being well shaken after each addition of the solution of soap, until a lather is formed of sufficient consistence to remain for five minutes all over the surface of the water, when the phial is placed on its side. The number of measures of soap solution is noticed, and the strength of the solution is altered, if necessary, by a further addition of either soap or spirit, until exactly 32 measures of the liquid are required for 100 measures of the water of 16 degrees of hardness. The experiment is made a second and a third time, in order to leave no doubt as to the strength of the soap solution, and then a large quantity of the test may be prepared ; for which purpose Dr Clark recommends to scrape off the soap into shavings, by a straight sharp edge of glass, and to dissolve it by heat in part of the proof spirit, mixing the solution thus formed with the rest of the proof spirit.

"(c) *Process for ascertaining the Hardness of Water.*—Previous to applying the soap test, it is necessary to expel from the water the excess of carbonic acid—that is the excess over and above what is necessary to form alkaline or earthly bicarbonates, this excess having the property of slowly decomposing a lather once formed. For this purpose, before measuring out the water for trial, it should be shaken briskly in a stoppered glass bottle half-filled with it, sucking out the air from the bottle at intervals by means of a glass tube, so as to change the atmosphere in the bottle ; 100 measures of the water are then introduced into the stoppered phial, and treated with the soap test, the carbonic acid eliminated being sucked out from time to time from the upper part of the bottle. The hardness of the water is then inferred directly from the number of measures of soap solution employed, by reference to the subjoined table. In trials of waters above 16 degrees hardness, 100 measures of distilled water should be added, and 60 measures of the soap test dropped into the mixture, provided a lather is not formed previously. If, at 60 test measures of soap test, or at any number of such measures between 32° and 60°, the proper lather be produced, then a final trial may be made in the following manner :—100 test measures of the water under trial are mixed with 100 measures of distilled water, well agitated, and the carbonic acid sucked out ; to this mixture soap test is added until the lather is produced, the number of test measures required is divided by 2, and the double of such degree will be the hardness of the water. For example, suppose half the soap test that has been required correspond to $10\frac{5}{10}$ degrees of hardness, then the hardness of the water under trial will be 21. Suppose, however, that 60 measures of the soap test have failed to produce a lather, then another 100 measures of distilled water are added, and the preliminary trial made, until 90 test measures of soap-solution have been added. Should a lather now be produced, a final trial is made by adding to 100 test measures of the water to be tried, 200 test measures of distilled water, and the quantity of soap test required is divided by 3 ; and the degree of hardness corresponding with the third part being ascertained by comparison with the standard solutions, this degree multiplied by 3 will be the hardness of the water. Thus, suppose 85·5 measures of soap-solution were required $\frac{8·55}{3}$ =28·5, and on referring to the table this number is found to correspond to 14°, which, multiplied by 3, gives 42° for the actual hardness of the water."

(*d*) Table of soap test measures corresponding to 100 test measures of each standard-solution :—

Degree of Hardness.	Soap Test Measures.	Differences as for the next Degree of Hardness.
0	1·4	
1	3·2	1·8
2	5·4	2·2
3	7·6	2·2
4	9·6	2·0
5	11·6	2·0
6	13·6	2·0
7	15·6	2·0
8	17·5	1·9
9	19·4	1·9
10	21·3	1·9
11	23·1	1·8
12	24·9	1·8
13	26·7	1·8
14	28·5	1·8
15	30·3	1·8
16	32·0	1·7

From this it appears that Dr Clark has adopted the indirect and not the direct way of registering hardness (or soap-destroying power). According to him the hardness of a water is measured by the quantity of carbonate of lime (or its equivalent in other salts) which the water contains, and not by the quantity of soap which a gallon of it will destroy.

Obviously, the indirect method of measuring hardness is only valid in so far as it is parallel with the direct way. As will be seen from the table for the reduction of soap-measures to their equivalent in carbonate of lime, there is a certain want of parallelism between the direct and indirect measurement of soap-destroying power. In order to bring this fact out distinctly, we repeat the table in an altered form. We have divided the number of soap-measures by 2, and thereby made the last term of the table alike for both carbonate of lime and corresponding soap-measures :—

Grains of Carbonate of Lime per Gallon.	Soap Test Measures.
0	0·7
1	1·6
2	2·7
3	3·8
4	4·8
5	5·8
6	6·8
7	7·8
8	8·75
9	9·7
10	10·65
11	11·55
12	12·45
13	13·35
14	14·25
15	15·15
16	16·00

It will be observed that the zero of carbonate of lime is opposite to 0·7 measure of soap test. What is the explanation of this? Obviously the gallon of pure water requires a certain amount of soap, and not infinitesimally little soap in order to yield a permanent lather. Dr Clark's degrees of hardness are grains per gallon of carbonate of lime or *its equivalent in soap-consuming power*. In the instance of pure water, the thing equivalent to carbonate of lime in soap-consuming power is the gallon of water.

According to the table, one gallon of pure water destroys as much soap in producing a lather as 0·8 grain of carbonate of lime would destroy if it were added to a gallon of water, which already contained, say, 10 grains of carbonate of lime, and a small quantity of soap test in excess over that required to neutralise the 10 grains of carbonate of lime.

Making the gallon of pure water count as the equivalent of 0·8 grain of carbonate of lime, we may rectify the table as follows :—

Grains of Carbonate of Lime (or matter equivalent to Carbonate of Lime) in a Gallon of Water.	Measures of Soap Test.
0·8	0·73
1·8	1·68
2·8	2·83
3·8	3·99
4·8	5·04
5·8	6·09
6·8	7·14
7·8	8·19
8·8	9·19
9·8	10·18
10·8	11·18
11·8	12·13
12·8	13·07
13·8	14·02
14·8	14·96
15·8	15·91
16·8	16·80

This table is derived from the foregoing by adding 0·8 grains to the carbonate of lime in every case, so as to correct for the soap-destroying power of the gallon of water; and every reading of soap test is multiplied by 1·05, so as to make the 16 measures into 16·80, and to increase the others in the same ratio.

This treatment of the table (and the logic of it will be evident on examination) exhibits the destruction of soap as very fairly parallel with the amount of carbonate of lime. We regard the departure from the parallel as within the limit of experimental error. From experimental data of our own we are inclined to rate the soap-destroying power of a gallon of pure water as equal to 1·0 grain, rather than 0·8 grain of carbonate of lime, and that will bring the numbers into closer approximation. We exhibit it. The factor used is 1·063.

Grains of Ca_2OCO_2 or its equivalent in a Gallon of Water.	Soap-Measures corresponding to the Ca_2OCO_2.
1	0·74
2	1·70
3	2·87
4	4·04
5	5·10
6	6·17
7	7·23
8	8·29
9	9·30
10	10·31
11	11·32
12	12·28
13	13·24
14	14·20
15	15·18
16	16·10
17	17·00

This table speaks for itself, and shows that the want of strict parallelism between the carbonate of lime and the soap-measures is due to experimental error solely. We may therefore get rid of the correction for supposed want of correspondence between the indications of hardness, as given by the carbonate of lime and as given by the quantity of soap consumed.

In place of making 16 (*or* 32) *measures of soap test to correspond to* 16 *grains of* Ca_2OCO_2 *in one gallon of water, make the measure* 17 (*or* 34) *of soap test, and the correction for want of correspondence will vanish.*

We prefer to make the standard solutions in a way somewhat different from that which was recommended by Dr Clark, as given in the passage above quoted.

We find it very convenient to keep a standard chloride of calcium solution (strength equivalent to 1 milligramme of carbonate of lime in a cub. cent. of solution).

This we prepare as follows:—Good chloride of calcium, prepared by dissolving a little marble in pure hydrochloric acid, is slowly heated to redness in a platinum crucible, which has been previously cleaned, ignited, and weighed. From 0·1 to 0·2 grm. of the chloride is taken. After heating the chloride of calcium to redness, the lid is put on to the crucible, and the whole cooled and weighed. The difference between the weight of the empty crucible and the weight of the crucible containing the chloride of calcium, which has been ignited, will be the weight of the chloride of calcium employed. Dissolve it in a little water, and, calculating from the known weight, make up with water, so as to get a solution of which one litre contains 1·110 grmme. of chloride of calcium. Each cub. cent. of this solution will, therefore, contain CaCl, equivalent to 1 milligramme of $CaOCO_2$. This standard-solution of chloride of calcium may, of course, if thought necessary, be verified with standard-solution of nitrate of silver (see Chlorine).

The basis of the system of standards is thus a standard-solution of chloride of calcium: strength 1 c. c. = 1 milligramme of carbonate of lime.

One of us has made the observation that in testing soap-solution against hard water, it is of no consequence whether the soap-solution be added to the hard water and the incipience of the lather be observed, or whether, conversely, the hard water be added to the soap-solution and the vanishing of the lather be observed. The vanishing point is just as sharp and quite as easy to recognise as the point at which lather begins to form.

Such being the case, there are various ways of working the soap test.

We next describe the way of making the *standard soap test.*

Take two parts of lead plaister and one of carbonate of potash, pound them well together, and exhaust repeatedly with alcohol of about 90 per cent., using altogether about thirty times as much alcohol as lead plaister. It will be found convenient to pound only small quantities of lead plaister and carbonate of potash at one operation. The soap-solution obtained, as just described, is a solution of potash soap, carbonate of lead being the complementary product. Before being used the soap-solution should be allowed to stand for some time, and then filtered. Before being standardised, it should be diluted with its own volume of water, and will then be still far too strong for use. The advantage of solution of potash soap over soda soap is, that it does not deposit continually, as soda soap is apt to do.

In order to standardise the soap-solution, and so make the *standard soap test*, so that 1 *cub. cent. is* equivalent to 1 *milligramme of carbonate of lime*, proceed as follows:—

Measure accurately say 10 c. c. of the unstandardised soap-solution, put it into a bottle with 70 c. c. of pure water, and then add the standard CaCl solution (strength 1 c. c. = 1 milligramme Ca_2OCO_2) until frothing stops, care being taken to shake up properly. From the result of the trial calculate how much dilution of the soap-solution is requisite in order to make 17 c. c. of the soap test consume 16 c. c. of the CaCl solution; dilute the unstandardised soap-solution accordingly with alcohol of 50 per cent. (proof spirit), and verify the standard soap test after it has been made up.

17 *c. c. of standard soap test should accurately neutralise* 16 *c. c. of standard CaCl solution in the presence of* 54 *c. c. of pure water.*

Each c. c. of the standard soap-solution will then be equivalent to 1 milligramme of carbonate of lime.

The use of this standard for ascertaining the degree of hardness of water will be plain from what has already been said. We give explicit directions as follows:—

Take 70 c. c. of the water and put it into a proper bottle. Add the standard soap test until lather is formed, and note down the number of c. c. of standard soap test required. Each c. c. of standard soap consumed indicates 1 grain of Ca_2OCO_2 (or its equivalent) in one gallon of the water.

Should 70 c. c. of the water require more than 17 c. c. of standard soap test, it will be requisite to dilute the water with its own volume of distilled water, and to subtract "1" from the number of c. c. of soap test used. This one is subtracted because the 70 c. c. of distilled water would themselves neutralise about 1 c. c. of soap. If after this addition, more than another 17 c. c. of soap test are required, another 70 c. c. of distilled water must be added, and another "1" subtracted from the number of c. c. of soap test, and so on, if a further addition is required. This dilution is required because it is not easy to observe the exact point of lathering when there is much curded soap present in relation to the volume of water.

If the result be desired in milligrammes of Ca_2OCO_2 in a litre of water, take 100 c. c. of the water, and each c. c. of standard soap will be equal to 10 milligrammes of Ca_2OCO_2 per litre. As in the former case, we must here dilute when a certain amount of soap test has been used, but in this case, as there is more water operated upon, we may use more soap test before diluting, in the proportion—

$$70 : 100 :: 17 : x = 24{\cdot}3.$$

Therefore, when we have added about 24·3 of soap test without producing a lather, we must dilute with 100 c. c. of distilled water. But if 70 c. c. of distilled water requires 1 c. c. of soap test to form a lather, 100 c. c. will require 1·43 c. c. We must, therefore, deduct 1·4 from the number of c. c. of soap test for every time we are compelled to dilute.

A very neat way of taking hardness is as follows:—Take a known volume of unstandardised soap-solution and dilute it with 70 c. c. of pure water, and then note the number of c. c. of standard CaCl solution (1 c. c. = 1 milligramme Ca_2OCO_2) required to *stop* lathering. (The number of c. c. of CaCl solution must approximate to 16.) The number of c. c. of CaCl solution + 1 = the number of milligrammes of *potential* Ca_2OCO_2 required by the volume of soap. (The "1" is for the 70 c. c. of water.) Then take the same volume of soap-solution, and add it to 70 c. c. of the water to be examined. *If a lather forms,* note how many c. c. of standard $CaCl$ solution are required to *stop lathering.* (The difference between the number of milligrammes of Ca_2OCO_2 required to stop lathering, and the potential Ca_2OCO_2 before named, is the hardness of the water in grains of $Ca\,OCO_2$ per gallon. *If a lather does not* form on the addition of the 70 c. c. of water, add another volume of the soap test, and 70 c. c. of distilled water (which will count as 1 milligramme of carbonate of lime).

An example will make this plain.

Took one measure of soap-solution, added 70 c. c. of distilled water, and noted that it required 14 c. c. of standard $CaCl$ solution to stop lathering. Therefore potential Ca_2OCO_2 required by the measure of soap-solution = 15 milligrammes.

Took one measure of soap-solution. It did not lather with 70 c. c. of the sample of water. Added a second measure of soap-solution, and 70 c. c. of distilled water; it gave a lather. Added standard $CaCl$ solution; 5 c. c. stopped formation of lather.

Total potential Ca_2OCO_2, . . = 30
(1 + 5) . . . . . = 6

Therefore one gallon contains of Potential Ca_2OCO_2. 24 grains

Temporary and Permanent Hardness.—The total hardness is the soap-destroying power of the water before boiling, or, indeed, before any treatment *of any kind.* The *permanent* hardness is the hardness after an hour's boiling, there being, of course, an addition of distilled water to make up for the loss on evaporation. During boiling, bicarbonate of lime is decomposed, the carbonate being deposited, and so the water becomes softer. The *temporary* hardness is the difference between total and permanent hardness.

HARDNESS OF WATER (*examples*).

	Ca_2OCO_2, or its equivalent in Soap-destroying Power.	
	Grains per Gallon.	Milligrammes per Litre.
Thames above London . (total),	14·0	200
New River, London . (total),	15·6	223
Bala Lake . . (total),	0·28	4
Bala Lake . (permanent),	0·21	3
Batchworth Spring Water (Chalk), (total),	17·6	
Same, after being softened by Dr Clark's process (*vide* Clark and Smith's paper), . . .	2·6	

In this table of examples we have given Clark's degrees of hardness, having copied the numbers from published papers. In order to translate Clark's degrees into "*potential carbonate of lime*," we add one. Thus 14·0 is the degree given in the table for Thames water, and 15·0 is the number of grains of *potential carbonate of lime* in a gallon of Thames water. In like manner, 1·28 is the number for Bala Lake, &c. The number of grains of potential carbonate of lime is strictly proportional to the soap-destroying power of the water.

Sometimes the hardness of water is not due to dissolved salts, but to the presence of free acid. We have met with two cases of this kind, both from manufacturing districts. The greater part of the hardness in these cases was due to free hydrochloric acid. In a case of this kind, add litmus and then standard caustic soda until the red colour of the litmus begins to change; boil when the colour will change to blue. Then titrate back with standard acid.

The acid employed contained 4·9 grammes per litre sulphuric acid (H_2SO_4), and the soda was of corresponding strength.

First case,—rain-water from a roof near soda-works.

Took 250 c. c., added litmus and then caustic soda; after adding 4·9 c. c. the colour began to change; boiled, colour changed to blue. Added standard acid two or three drops at a time, boiling between each addition until the colour again changed, required 0·4 of acid. The water had therefore neutralised 4·5 c. c. of soda. 1000 c. c., or a litre, would therefore require 17 c. c. Each c. c. = 3·65 milligrammes hydrochloric acid. The water contained therefore 62·05 milligrammes hydrochloric acid per litre of $4\frac{1}{3}$ grains per gallon.

Second case,—250 c. c. required 7·2 c. c. soda.

One litre, therefore, contained 104 milligrammes of hydrochloric acid, or $7\frac{1}{4}$ grains per gallon.

It is often requisite to titrate waters that contain carbonates dissolved in them, together with an excess of carbonic acid. In such cases, titrate directly with sulphuric acid and litmus in the boiling liquid.

INDEX.

KOUMISS.

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KOUMISS, a sparkling milk wine prepared of the best milk, has now, after four years' trial in this country, established its great reputation as the most valuable alimentary and tonic beverage in all states of catarrh or relaxation of the mucous membranes when accompanied by loss of strength and flesh. The Lactic and Carbonic Acids and Alcohol, together with a minute quantity of certain fragrant associates, are so combined in the Koumiss as to stimulate the stomach and nervous centres "*without affecting the head.*" A large quantity of very assimilable food can thus be taken by the feeblest stomach, especially as the caseine of the milk is so finely divided as to form, with the Carbonic Acid, a rich attenuated foam, and to predispose the other constituents to rapid transformation into lymph and blood. Fresh milk, even when mixed with spirits and soda-water, coagulates within the stomach into thick clots, and irritates it; whereas in the Koumiss the double process of fermentation has done nearly all the preliminary work which would fall otherwise on the digestive organs; and these physical and chemical characteristics of Koumiss render it so invaluable in the treatment of *debility and emaciation.* The Lactic Acid it contains is a prime constituent of the gastric juice, and the state of vitality of the Koumiss (being a *fermenting* and not a fermented beverage!) gives it the property of greatly assisting digestion and assimilation.

According to Russian, German, and our own medical authorities, it is settled beyond question that "*Koumiss is wonderfully suited as a form of nourishment for badly nourished, wasted, rachitic, or scrofulous children, or for convalescents;* and also that it can often cure cases of *obstinate chronic diarrhœa, or old catarrh.*" See for this, and Wanklyn's chemical analysis of our various sorts of Koumiss, The Irish Hospital Gazette, December 15th, 1873; The British Medical Journal of January 3d, 10th, February 21st, and March 7th, 1874; Pharmaceutical Journal, February 28th, March 21st; and The London Medical Record, April 1st.

Our own small pamphlet, with analysis, testimonials, prices of our articles, and all other informations, may be had gratis on application to our Manufactory in London,

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MANUFACTURERS OF SPARKLING KOUMISS AND BLAND,

Importers of Natural Mineral Waters, &c.

Amongst the many spontaneous testimonials on view at our office, we insert the following :—

October 27, 1871.

DEAR SIR,—Many thanks for your letter. I have myself begun to give a fair trial to Koumiss in a young lady, who is dreadfully phthisical. She has taken Koumiss for sixteen days, and the change it has occasioned has been most remarkable; she has gained flesh, her cough has diminished, and her complexion has become wonderfully clear and bright. I shall put another patient under Koumiss in a day or two,—Yours, &c.,

EDWARD CHARLTON, M.D.,
Senior Physician of the Infirmary of Newcastle-on-Tyne, and Lecturer on Practice of Physic in the College of Medicine; late President of the British Medical Association, &c. &c.

March 10, 1874.

Dr Myrtle, of Harrogate, Yorkshire, writes :—"I gladly bear witness to the value of this article of diet (Koumiss), and look upon it as one of the most important additions which have been made to the physician's repertorium. It is quite as much a true therapeutic agent as a genuine food, and is capable of being successfully employed in cases where the stomach can neither do with food of the ordinary kind or physic."

LONDON, *October* 11, 1872.

Milk has been justly called the typical food, and is eminently fitted for children; but for adults, and all those who not unfrequently cannot take milk, Koumiss is its true representative. The caseine and fat contained in Koumiss are in a state of fine division, and in a very favourable condition for digestion. The presence of the lactic and carbonic acids, and small quantities of alcohol, is, in my opinion, conducive to easy assimilation. The earlier forms of Koumiss form agreeable beverages.

F. ALFRED WANKLYN, M.R.C.S.,
Corresponding Member of the Royal Bavarian Academy of Sciences; Public Analyst for Buckinghamshire, Buckingham, and High Wycombe.

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9 ARUNDEL TERRACE, BRIGHTON, *November* 13, 1872.

I have been an invalid for the last twelve years, suffering from an affection of the heart, lung, &c. I have consulted some of the first physicians in Europe, and tried the most approved remedies; but I can with the greatest truth state that I have derived more benefit from a pint of the Medium Koumiss at breakfast, lunch, and dinner, than from any other medicine, or diet, that I have previously taken. I have gained ten pounds in weight in eleven months. My wife and my son are also taking it with great benefit. I have recommended it to many of my patients with great advantage, &c.

RICHARD DAWSON, M.D., M.R.C.S., and L.R.C.P., Lond.

LONDON, *April* 4, 1871.

Koumiss is a very assimilable nutritious food and potent medicine in close natural union. I have lived on Koumiss and bread, almost exclusively, for the last six months, with great comfort and increase of weight, after having been very much reduced in health and strength. Its genuine worth entitles it justly, therefore, to the popular favour which it continues to gain in Europe and Great Britain.

CAMPBELL MORFIT, M.D., F.C.S., &c.

---

10 CHANDOS STREET, CAVENDISH SQUARE, W.,
LONDON, *May* 25, 1874.

A preparation from genuine cow's milk, called "Koumiss," has now for some time attracted my attention. At first I was sceptical as to the benefits which were said to result from its consumption, but a somewhat extended experience has thoroughly convinced me of its great value. In cases where nutrition fails, when strength and weight are being lost, the virtues of the Koumiss soon become evident; the appetite improves, and the patient experiences a considerable increase of constitutional power. In cancerous destructions and other diseases of the large intestine I have found Koumiss of eminent utility, and can thoroughly recommend it to my professional brethren.

WM. ALLINGHAM, F.R.C.S.,
Surgeon to St Mark's Hospital for Fistula and other diseases of the Rectum, Consulting Surgeon to the British Orphan Asylum, &c. &c.

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8 WEYMOUTH STREET, PORTLAND PLACE, W.,
LONDON, *May* 20, 1874.

The various sorts of Koumiss manufactured by the firm of E. Chapman and Co., London, W., have given great satisfaction to me and others in the treatment of anæmia, weakness of digestion and assimilation, emaciation, catarrh of the mucous membranes, in pharyngitis, laryngitis, bronchitis, and pneumonia, sometimes even at the most critical stages of disease and of diminished vital power. In chronic syphilis, scrofula, and other constitutional cachectic conditions of the body, but especially in the early stage of consumption, I rely upon Koumiss as the "first" amongst all remedies used for their treatment; it improves nutrition, raises strength, and alters the constitution advantageously.

A. V. JAGIELSKI, M.D.,
Member of the Royal College of Physicians, London, &c. &c.

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BLAND, the most agreeable and refreshing beverage, is made from milk upon a similar principle as Koumiss, so as to render it a valuable tonic stimulant. By its use the digestive organs are improved. The ginger, which is used chiefly as a flavouring, adds an aromatic and carminative property; but we prepare the Bland also with lemon, orange, and almond flavours. The medical profession recommend its use particularly during inflammatory and febrile diseases. It may also be mixed with wine, spirits, and beer advantageously. The Bland will keep good for an indefinite period.

OUR SCENTED GLYCER-AMYGDALINE CREAM

Is a really useful addition on every Toilet-Table.

During a cold, and in *rheumatic* affections, it may be applied with benefit to the forehead, nose, chest, neck, or any other painful locality.

As a cosmetic it is very efficacious in rendering the skin soft and delicate, and it is quite unequalled for imparting a fresh and healthy colour to the face and lips. For the hands it is best employed at night, and with gloves on during the night.

On the hair, moustache, whiskers, beard, it may be used as a pomade. It keeps them moist, soft, and in good appearance, besides promoting their growth.

WARSAW GLYCERINE SOAP, 6s. per Dozen Cakes, or 6d. per piece.