

## PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXX.—*On some Points in the Analysis of Potable Waters.*

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EIGHT years have now elapsed since, in conjunction with Dr. Armstrong, I had the honour to lay before the Fellows of the Chemical Society (*Jour. Chem. Soc.*, xxi, 77), an account of the chief determinations of water analysis. That account recorded the results of observations and experiments extending over more than two years, and embracing a thorough examination of the methods then employed in the analysis of potable waters, especially of the four processes used for the estimation of the organic constituents, viz.:—The “ignition,” “permanganate,” “albuminoid ammonia,” and “combustion” methods. This examination showed conclusively that the last-named process was the only one yielding quantitative results in any degree trustworthy. The combustion and collateral processes then recommended have since been tested by many thousands of analyses of waters from the most widely different sources, and I therefore venture again to return to the subject, and to communicate to the Society the results of this enlarged experience. I do this with the less hesitation, because the further my inquiries into the influence of water upon the public health have extended themselves, the more have they convinced me that this technical application of chemical analysis is second to none in importance to the community at large. In the interests of the public health, and for the credit of applied science, the improvement of this branch of analysis is, in my opinion, worthy of the greatest efforts of chemists, and it is the hope of attracting increased attention to accurate, as distinguished from fallacious, processes in water analysis that has induced me to make this communication.

The two chief objects to be kept in view in the analysis of potable water are, firstly, the discovery of the evidence of *past* pollution by organic matter, and, secondly, the quantitative determination of *present* or *actual* organic impurity.

With regard to the methods for attaining the first of these objects, I have nothing to add to the descriptions given in the paper already referred to; but considerable difference of opinion having been expressed as to the importance of knowing the past history of any sample of water, as regards its pollution by organic matter, and even as to the possibility of ascertaining it with any degree of certainty, I may here

be permitted to illustrate these points by the results of a more extended experience.

The past history of a water is made out chiefly through the mineral products of oxidation which the polluting organic matters have yielded, and which are still present in the water. Now these products are innocuous, and therefore it is obvious that if all kinds of organic matter behaved alike under the influence of oxidizing agents, such evidence of previous pollution might be safely disregarded; but it is almost superfluous to point out that there are wide differences between various kinds of organic matter, in regard to the rapidity with which they combine with oxygen; and of all kinds, that which is organised and living, opposes by far the greatest obstacles to oxidation. The researches of Chauveau, Burdon Sanderson, Klein, and others, scarcely leave room for doubt that the specific poisons of the so-called zymotic diseases consist of organised and living organic matter, and it is now certain that water is the medium through which some at least of these diseases are propagated. It is evident, therefore, that an amount of exposure to oxidizing influences which may resolve the dead organic matters, present in water, into innocuous mineral compounds, may and probably will fail to affect those constituents which are endowed with life. Indeed, instances are not wanting illustrative of the persistency of the typhoid and other similar poisons when they are diffused in water and then exposed to oxidising influences. One of the most striking of these occurred at the village of Lausen, near Basel, Switzerland.\* It was investigated with much care and skill by Dr. A. Hägler, of Basel. In this healthy village, which had never, within the memory of man, been visited by epidemic typhoid, and in which even a single sporadic case had not occurred for many years, there broke out in August, 1872, an epidemic which simultaneously attacked a large proportion of the inhabitants. About a mile south of Lausen, and separated from it by the mountainous ridge of the Stockhalden, which is probably an old moraine from the glacial epoch, lies a small parallel valley—the Fürlerthal. In an isolated farmhouse situated in this valley, a farmer, who had just returned from a long journey, was attacked by typhoid fever on the 10th of June. During the next two months, three other cases occurred in the same house, viz., a girl who was attacked on the 10th of July, and the farmer's wife and their son, who sickened in August. The inhabitants of Lausen were entirely ignorant of what had occurred at this solitary mountain farm, which was cut off from all communication

*Deutsche Vierteljahrsschrift für öffentliche Gesundheitspflege*, Bd. vi, s. 154, and 6th Report of the Commissioners appointed in 1868 to inquire into the best means of preventing the pollution of rivers, p. 463.

with the rest of the world; when, on the 7th of August, ten of the villagers were suddenly struck down by typhoid fever, whilst during the next nine days the number of cases had already increased to 57 out of a population of 780 persons living in 90 houses. In the first four weeks, the number of cases reached 100 (or above 12 per cent. of the population); and altogether to the close of the epidemic at the end of October, 130, or 17 per cent. of the population were attacked, besides 14 children who were infected at Lausen during their summer holidays, and became ill after their return to schools in other localities.

The fever cases were pretty equally distributed throughout the entire village, but those houses, six in number, which were supplied with water from their own private wells, and not from the public fountains, were entirely exempt. This remarkable difference naturally led to a suspicion that the public water supply was connected with the cause of the epidemic, although the apparently immaculate source of this supply seemed to negative any such suspicion. The water came from a spring situated at the foot of the adjacent Stockhalden ridge. It was there received in a tank lined with brickwork, and carefully protected from pollution; nevertheless, a careful investigation into the source of this spring placed beyond all doubt the origin of the infection. Ten years previously, it had been proved that direct water communication through the intervening mountain existed between the spring, and a brook in the Fürlerthal flowing past the farmhouse in which the typhoid cases occurred. At that time there was spontaneously formed, by the giving way of the soil at a short distance below the farmhouse and close to the brook, a hole about 8 feet deep and 3 feet in diameter, at the bottom of which a moderate stream of clear water was observed to be flowing. As an experiment, the whole of the brook water was now diverted into this hole, at the bottom of which it entirely disappeared, but in an hour or two the spring at Lausen, at that time nearly dry from a long drought, overflowed with an abundance of water which was turbid at first, but afterwards clear, and this continued until the Fürler brook was again confined to its bed. It was, however, afterwards noticed that whenever the meadows below this hole were irrigated with the water of the Fürler brook, the volume of the Lausen water-supply became greatly augmented a few hours afterwards. Now this irrigation, practised every year, was carried on in the summer of the epidemic from the middle to the end of July, the brook being polluted by the dejections of the typhoid patients, for it was in direct communication with the closets and dungheaps of the infected house, whilst all the chamber-slops were emptied directly into it, and the dirty linen of the patients washed in it. Soon after the irrigation had begun, the water supplied

to Lausen was at first turbid, acquired an unpleasant taste, and increased in volume. About three weeks after the commencement of the irrigation, the sudden explosion of typhoid fever in Lausen occurred.

In his search after the cause of this outbreak, Dr. Hägler did not rest satisfied with the evidence just recorded, but supplemented it by the following ingenious and conclusive experiments :—The hole in the Fűrlerthal, already mentioned, was re-opened, and the brook again led into it : three hours later, the fountains of Lausen delivered double their previous supply of water ; 18 cwts. of common salt previously dissolved in water were now poured into the hole, and soon the water at Lausen exhibited a stronger chlorine reaction, gradually increasing until it became very strong, whilst the proportion of solid matter dissolved in the water augmented three fold. The passage of the Fűrlerthal water to the fountains of the fever-stricken village was thus established beyond doubt, but another interesting question here presented itself ; did the water find its way through the Stockhalden by a natural open conduit, or was it filtered through the porous material of the old moraine ? To decide this point,  $2\frac{1}{2}$  tons of flour were first carefully and uniformly diffused in water, and then thrown into the hole, but neither an increase in the solid constituents nor the slightest turbidity of the Lausen water was observed after this addition.

Thus the investigation of the typhoid epidemic at Lausen showed :—

1. That the epidemic followed immediately after the use, for dietetic purposes, of water which had received the dejections of persons suffering from typhoid fever, and that it was confined to persons who drank the infected water.

2. That the water still retains its infective properties after a filtration, which is efficient enough to remove very minute starch granules, but not sufficient at all times, to prevent the passage of visible suspended matter in a still more minute state of division.

3. That spring water which has been polluted with human excrements before its descent into the earth, and which is subject to visible turbidity, is not always safe for domestic use.

4. That water which is polluted with *normal*, as distinguished from *infected*, excrementitious matters of human origin, may be used for dietetic purposes with impunity.

Inasmuch, therefore, as no means are known of distinguishing between normal and infected excrements, and as excrementitious matters are liable to become infected constantly with typhoidal, and occasionally with cholera poison, it is not safe to consume water which is contaminated with human dejections. Further, as typhoidal poison is almost certainly organised and living, it is likely to resist oxidation

much longer than the dead organic matters with which it is associated ; and as this poison is not removed from water by natural filtration through nearly a mile of porous earth, it follows that the tracing of the previous history of potable water is of prime importance in water analysis.

The method of estimating and expressing in a concrete form the previous sewage or animal contamination of a sample of water, was fully described in the paper by Dr. Armstrong and myself already alluded to ; and, as the result of long experience, I have very rarely found that this estimation casts any suspicion upon water of really good quality. Thus out of 195 samples of upland surface water which have been examined, there were only 20 which contained, in the form of nitrates, nitrites, and ammonia, more nitrogen than is present in these forms in rain water ; and in each of the 20 cases the excess was very slight, and the water was not obtained from such a source as to preclude altogether animal pollution. Again, out of 21 samples of spring water from indisputably unpolluted sources, there were only two which contained in 100,000 parts more than  $\cdot 032$  part of nitrogen in the form of nitrates, nitrites, and ammonia. These were both taken from a very small spring known as St. Boniface's Wishing Well. The spring issues from the steep slope on the south side of St. Boniface Down, Ventnor, Isle of Wight, about 100 feet below the summit of the down. The first sample was taken on November 16th, 1872, when the spring was scarcely running two gallons per hour : 100,000 parts of this sample contained  $\cdot 083$  part of nitrogen in the form of nitrates, nitrites and ammonia. The second sample was collected on March 8th, 1873, when the issue of water was at least twenty fold as great as on the former occasion. This sample contained  $\cdot 061$  part of nitrogen as nitrates, nitrites, and ammonia, in 100,000 parts of water. Several explanations of this abnormal excess of nitrogen in the forms just specified offer themselves. In the first place, the upper part of Boniface Down is occasionally pastured by sheep and cattle ; secondly, chalk naturally contains fossil animal remains, in which all organic matter is probably not oxidised ; and thirdly, the nitrogen compounds in the rain falling upon Boniface Down may undergo concentration, by the evaporation of a considerable proportion of the water from the spongy surface of the chalk. Considerable support is given to the last explanation by the fact, that the proportion of chlorine as chlorides (which are chiefly derived from sea spray), is very high, viz., 6·4 parts in 100,000 parts of water in the autumn, and 7·4 parts in the spring sample, whilst the proportion in springs at the base of the down and nearer the sea is only from 3 to 3·6 parts in 100,000 parts of water. In summer and autumn the deposit of sea spray would be small, and the evaporation great, whilst in winter and spring the

deposition of sea spray would be copious, and the evaporation comparatively small. This would explain on the one hand the occurrence of a larger proportion of nitrates, and a somewhat smaller proportion of chlorides in the autumn sample, and on the other, the presence of a smaller proportion of nitrates, and a somewhat larger one of chlorides in the spring sample.

The occurrence of nitrates in minute quantity, in the earth of unmanured forest land, observed by M. Bousingault, was probably due to the evaporation of rain water from the surface of the soil, and the concentration of nitrates in the upper layers.

As the result of long experience in connection with the occurrence of nitrates, nitrites, and ammonia in potable waters, I am of opinion that the presence of nitrogen in these forms in water, in quantity above that which can be derived from rain, is reasonably safe and trustworthy evidence of the previous pollution of that water by animal matters.

On the other hand, it must not be forgotten that the absence of nitrogen in these forms is not absolutely conclusive evidence of immunity from such pollution. There are several agencies at work by which this testimony, as to the amount of animal matter previously in the water, may be weakened or altogether destroyed. Thus we look in vain for the full evidence of previous animal pollution, in the effluent water from fields irrigated with sewage; because the growing plants have removed a considerable proportion of ammonia, nitrates, and nitrites, from the liquid as it flows amongst their rootlets. In like manner the aquatic vegetation of rivers, lakes, and reservoirs slowly removes these compounds from water, and to that extent destroys the evidence of anterior animal contamination. Nitrates and nitrites are also rapidly destroyed when the organic matter in the water containing them enters into putrefaction,—a condition which often occurs in streams or reservoirs containing much polluting organic matter. It again not unfrequently takes place in water-bearing strata far removed from the surface, although the water in this case may contain but a comparatively small amount of organic matter; the latter, however, cut off from a supply of atmospheric oxygen—as in the chalk beneath the London clay for instance—accomplishes its oxidation at the expense of the nitrates or nitrites, and thus destroys them. Owing to this cause, the evidence of previous animal contamination is not met with in the water of some deep wells, in which it might otherwise be expected to occur.

The previous animal contamination of water, as deduced from chemical analysis, must therefore always be regarded as a minimum quantity; it does not denote the *comparative* freedom of different samples of water from anterior pollution, but whenever analysis shows

this excess of nitrogen in the shape of nitrates, nitrites, and ammonia, the water stands convicted of previous contamination, at least to the extent so indicated.

The meaning of the expression "previous sewage or animal contamination" may easily be misconstrued, unless an explanation accompanies analytical reports upon waters exhibiting such contamination. I have, therefore, for many years past, sent a copy of the following explanation with every such report; and when the water contains actual sewage or animal contamination, the words printed in italics in the fifth paragraph are erased.

#### "DRINKING WATER.

##### *Previous Sewage or Animal Contamination.*

There is reason to believe that the excrementitious matters which exist in sewage are often possessed of intensely infectious properties; and that sewage mixing with water, even in the minutest proportion, is likely, by such properties, to spread particular diseases among populations which drink the water.

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

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

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

The column headed "Previous Sewage or Animal Contamination," in the accompanying analytical table, expresses, in terms of average London sewage, the amount of animal matter with which 100,000 lbs. of each water was, at some time or other, contaminated. Thus 100,000 lbs. of the water of  
 had been polluted with an amount of animal matter equal to that contained in                    lbs. of average London sewage. *So far as chemical analysis can show, the whole of this animal matter had been oxidised and converted into mineral and innocuous compounds at the time the analysis was made; there is, however, always a risk lest some portion (not detectable by chemical or microscopical analysis) of the*



*noxious constituents of the original animal matters, should have escaped that decomposition which has resolved the remainder into innocuous mineral compounds. But this evidence of previous contamination implies much more risk, when it occurs in water from rivers and shallow wells, than when it is met with in the water of deep wells or of deep-seated springs. In the case of river water there is great probability that the morbid matter, sometimes present in animal excreta, will be carried rapidly down the stream, escape decomposition, and produce disease in those persons who drink the water; as the organic matter of sewage undergoes decomposition very slowly, when it is present in running water. In the case of shallow-well water, the decomposition and oxidation of the organic matter are also liable to be incomplete during the rapid passage of polluted surface water into shallow wells. In the case of deep-well and spring water, however; if the proportion of previous contamination do not exceed 10,000 parts in 100,000 parts of water, this risk is very inconsiderable, and may be regarded as nil, if the direct access of water from the upper strata be rigidly excluded; because the excessive filtration to which such water has been subjected, in passing downwards through so great a thickness of soil or rock, and the rapid oxidation of the organic matters contained in water when the latter percolates through a porous and aerated soil, afford a considerable guarantee that all noxious constituents have been removed.*

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

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

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

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

*Reasonably Safe Water.*—Water, although it exhibits previous sewage or animal contamination, may be regarded as reasonably safe when it is derived either from deep wells (say 100 feet deep), or from deep-seated springs; provided that surface-water be rigidly excluded



from the well or spring, and that the proportion of previous contamination do not exceed 10,000 parts in 100,000 parts of water.

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

*Dangerous water* is, 1st, shallow-well, river, or flowing water, which exhibits more than 20,000 parts of previous animal contamination in 100,000; 2nd, shallow-well, river, or flowing water containing less than 20,000 parts of previous contamination in 100,000 parts; but which is known, from an actual inspection of the well, river, or stream, to receive sewage, either discharged into it directly, or mingling with it as surface drainage. 3rd. As the risk attending the use of all previously contaminated water increases in direct proportion to the amount of such contamination, deep-well or deep-seated spring water exhibiting more than 20,000 parts of previous contamination in 100,000 must be regarded as dangerous.

River or running water should only be placed in the second class provisionally, pending an inspection of the banks of the river and tributaries; which inspection will obviously transfer it either to the class of reasonably safe water, if the previous contamination be derived exclusively from spring water, or to the class of dangerous water, if any part of the previous contamination be traced to the direct admission of sewage or excrementitious matters."

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The *actual*, or present, as distinguished from the *past* polluting organic matter of potable water, can only be estimated from the amount of carbon and nitrogen found as constituents of the organic matter present in the water when the analysis is made. The mode of determining this organic carbon and nitrogen has been already fully described by Dr. Armstrong and myself. We have shown that by measuring these elements as carbonic anhydride and nitrogen gases, one-millionth of a gramme of nitrogen and half a millionth of a gramme of carbon are distinctly measurable quantities. We also tested the method, by adding weighed quantities of various organic matters to known volumes of pure water, and submitting these artificially prepared waters to analysis.

In ten such determinations of organic carbon, the errors never reached  $\frac{1}{10}$ th of the total amount of carbon present, and averaged only  $\frac{1}{25}$ nd. Errors of this magnitude, although they would be fatal in the determination of a complex molecular formula, have scarcely any appreciable effect upon the judgment of an analyst respecting the

quality of a sample of water. Six determinations of organic nitrogen were similarly made. One of these was bad, the error amounting to one-fourth of the amount of organic nitrogen present, but the maximum error in the remaining five was only  $\frac{1}{17}$ th, and the average was less than  $\frac{1}{80}$ th. These errors, like those made in the case of organic carbon, would have no appreciable import in judging of the quality of a sample of potable water.

It is therefore evident, that this method of determining organic carbon and nitrogen, as described in your journal eight years ago, was fully equal in delicacy and certainty to all the requirements of water analysis; but, as was then pointed out, it needed considerable care on the part of the operator, and it was necessary to conduct the evaporation of the water under discs of filter paper, in an atmosphere kept as free as possible from ammonia,—precautions which required the use of a room from which most of the ordinary laboratory operations were excluded. These inconvenient restrictions have long since been removed, and every part of a water analysis can now be performed with certainty and success in any laboratory fitted for the ordinary determinations of quantitative analysis; and I have here to express my thanks to Mr. W. Thorp, late chief assistant in the Rivers Commission laboratory, for the important and conscientious aid which he, for many years, afforded me in the progressive improvement of this process. Moreover, the time required for evaporation has been reduced by two-thirds, or even more, by the adoption of a simple contrivance devised by Professor Bischoff, and the risk of contamination during evaporation has been entirely obviated by a method devised by me for distilling off the water from the residue in a confined portion of air. These improvements have also secured greater accuracy in the determinations, and, without gross carelessness, errors of the magnitude just mentioned cannot now occur. Instead, however, of mentioning each improvement which has been effected, it will be preferable to describe the whole process of determining organic carbon and nitrogen. Pour one litre\* of the sample of water into a suitable flask; add 15 c.c. of a saturated solution of sulphurous acid in pure water, and boil the mixture briskly for a few seconds in order to decompose the carbonates present. The sulphurous anhydride, which is used for the preparation of the solution of sulphurous acid, must be made from copper clippings and *pure* sulphuric acid, in order that it may be free from nitrogenous compounds. Evaporate the acidulated and boiled water to dryness in a hemispherical glass dish about one decimetre in diameter, placed in a copper capsule, surrounded by a loose flanged cylinder of copper, which carries a glass shade about

\* In the case of waters much contaminated by organic matter half, or even a fourth of a litre is sufficient.

12 inches high, and of suitable diameter. The capsule is heated by a water-bath, as shown in the annexed drawing (fig. 1):—*aa* is the copper capsule in which the glass dish, *bb*, is heated, *cc* is the copper ring or cylinder, 80 mm. high; it is provided at its upper edge with a rim or flange of the same diameter as that of the copper capsule, so that the glass shade, *d*, may rest on either. The water to be evaporated is conducted from the flask in which it was boiled, to the glass evaporating dish by a self-supplying apparatus, *e*, *f*, *g*. The neck of

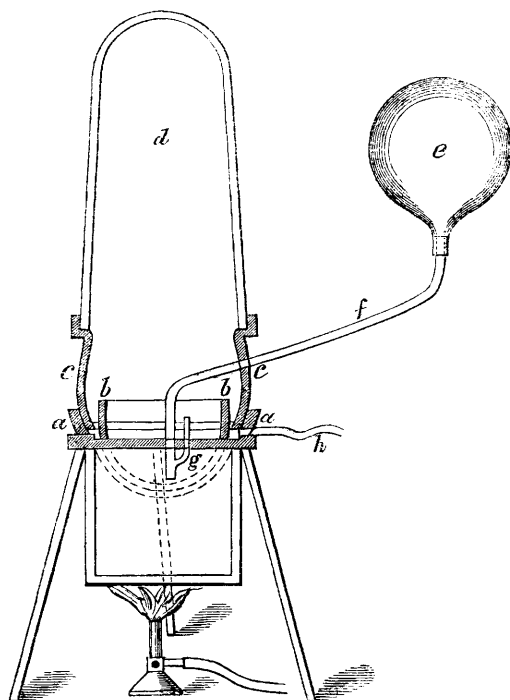


FIG. 1.

the flask, *e*, is ground so accurately into the enlarged end of the glass tube, *f*, of about 8 mm. internal diameter, as to be water-tight without the use of grease. The tube close to the enlarged end is bent at an angle of about 120°. The other end of the tube, which is formed into the usual self-supplying apparatus, *g*, is again bent so as to be parallel with the enlarged end of the tube. The acidulated water having been boiled in the flask and allowed to cool somewhat, the tube is attached, the apparatus inverted and introduced through a slit in the upper edge of the copper cylinder into the glass dish, without, however,

touching the bottom. The slit should be so deep that the shade does not quite touch the glass tube. When the flask is nearly empty, the copper cylinder and self-supplying apparatus may be removed, the remainder of the water poured into the dish, and the glass shade placed directly on the copper capsule. To ensure the destruction of nitrates add one drop of a concentrated solution of ferric chloride to the first dishful. The condensed water, which trickles from the glass shade, collects in the space between the glass dish and the copper capsule, and then flows off through the syphon tube, *h*. In this way the evaporation of a litre of water occupies from 24 to 26 hours; that is to say, with a constant gas-flame and self-supplying water-bath, if the evaporation be commenced in the forenoon, the residue can be burnt in the afternoon of the following day. If the water contains very large quantities of nitrates or nitrites, their reduction and the dissipation of their nitrogen requires the use of a larger quantity of sulphurous acid than that just mentioned; thus, when the nitrogen as nitrates and nitrites exceeds 0.5 part in 100,000 parts of water, the glass dish, containing the solid residue left on evaporation, must be filled with pure water containing one-tenth of its volume of a saturated solution of sulphurous acid, and the evaporation again carried to dryness; if it exceeds 1 part, a quarter of a litre of this solution should be evaporated on the residue; 2 parts, half a litre; and if 5 parts of oxidised nitrogen be present, one litre. In the ordinary course of analysis, the nitrogen as nitrates and nitrites will have been determined before the evaporation of the litre of water is finished.

The next operation is the combustion of the organic matter in the solid residue left on evaporation. This must be performed in a tube of the hardest Bohemian glass, and preferably of rather smaller diameter than that usually employed in organic analysis. A piece of this tube about 18 inches long is to be carefully washed, rinsed with distilled water, dried in an oven, and one end closed before the blowpipe. The oxygen is supplied by granulated cupric oxide, which must be made by roasting thin sheet copper, or preferably oxidised copper, (procurable from the sulphate of copper manufacturers) in a muffle or inclined iron tube.\* Cupric oxide made from the nitrate is entirely useless for this process. Place the glass dish containing the dry residue upon a sheet of glazed paper, then add to the contents of the dish a few grammes of powdered cupric oxide, and with a small elastic steel spatula carefully remove the residue from the sides, and mix it intimately with the cupric oxide. Now put into the combustion tube about 1 inch of the granulated cupric oxide, and

\* Before use, a sample of this cupric oxide should be assayed in a blank combustion. It should yield only a very minute bubble of gas which ought to be almost entirely absorbed by potassic hydrate.

transfer, in the usual manner, the contents of the glass dish to the tube, rinsing out the former twice with small quantities of powdered cupric oxide, and transferring the rinsings to the tube. Fill up to a distance of 10 inches from the closed end of the tube with granulated cupric oxide, then put in a cylinder of fine copper gauze 3 inches long, made by rolling the gauze round a copper wire. This cylinder must, before use, be first oxidised in air and reduced in hydrogen as usual. In front of the gauze put about 1 inch of granulated cupric oxide. This last is required to oxidise traces of carbonic oxide, always formed by the reducing action of impurities in the copper gauze.

The open end of the tube must now be drawn out, so as to contract it to one-fifth of an inch in diameter for about 4 inches of its length, and the tube is then ready to be placed in the combustion furnace, and attached to the Sprengel pump by a caoutchouc and glycerin joint. After the furnace around the front end of the combustion tube is lighted, the pump is to be worked until the tube is exhausted as completely as possible,—an operation which requires from five to ten minutes. The flow of mercury is then stopped.

The inverted tube filled with mercury destined to receive the gaseous products of combustion having been placed over the recurved delivery end of the pump, the combustion is to be conducted in the usual manner, care being taken that when the organic matter begins to burn, the operation proceeds very slowly until the vacuum becomes considerably impaired. A combustion usually lasts from three-quarters of an hour to an hour; at its conclusion, unless the water residue contained much organic matter, no gas will have passed into the inverted tube. The pump must then be again set to work, and in from five to ten minutes the whole of the gases will be transferred to the inverted tube.

The gas collected consists of carbonic anhydride, nitric oxide, and nitrogen, which can readily be separated and determined by the ordinary processes of gas analysis as described in the *Journal of the Chemical Society*, vol. xxi, p. 109. From the quantity of nitrogen thus obtained there has to be deducted the amount of ammoniacal nitrogen present in the water, or rather this amount minus the loss incurred by the dissipation of ammonia during the evaporation of the water. Potable waters rarely contain so much as .01 part of ammonia in 100,000 parts, and then the loss of ammoniacal nitrogen during evaporation is too insignificant to require correction. Very impure waters and certain deep well waters, however, sometimes contain much larger proportions of ammonia, and then the loss on evaporation with sulphurous acid becomes very considerable, as is seen from the following table, which embodies the results of numerous experiments made with artificial waters containing known quantities of ammonia:—

*Parts in 100,000. Loss of Nitrogen by Evaporation of  $NH_3$ .  
[ $SOH_2$ .]*

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

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

The ammonia in strongly ammoniacal waters may be entirely dissipated during evaporation by substituting boracic acid or borax for sulphurous acid; but the simultaneous carbon determination must be rejected, as boracic acid does not completely decompose carbonates. A separate carbon determination, with sulphurous acid as the acidifying agent, is therefore necessary. The use of borax is recommended when great accuracy is required in the determination of organic nitrogen in strongly ammoniacal waters.

The following table, constructed from numerous experiments with artificial waters containing known weights of ammonia, gives the correction for loss of ammoniacal nitrogen when the water is acidified with phosphoric acid:—

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

Volume evaporated.	$NH_3$ per 100,000.	Loss of N. per 100,000.	Volume evaporated.	$NH_3$ per 100,000.	Loss of N. per 100,000.	Volume evaporated.	$NH_3$ per 100,000.	Loss of N. per 100,000.	Volume evaporated.	$NH_3$ per 100,000.	Loss of N. per 100,000.
100 c.c.	10.0	.483	100 c.c.	7.2	.386	100 c.c.	4.4	0.283	100 c.c.	1.6	.143
..	9.9	.480	..	7.1	.382	..	4.3	0.279	..	1.5	.137
..	9.8	.476	..	7.0	.379	..	4.2	0.275	..	1.4	.132
..	9.7	.473	..	6.9	.375	..	4.1	0.271	..	1.3	.127
..	9.6	.469	..	6.8	.372	..	4.0	0.267	..	1.2	.122
..	9.5	.466	..	6.7	.368	..	3.9	0.262	..	1.1	.117
..	9.4	.462	..	6.6	.365	..	3.8	0.257	..	1.0	.112
..	9.3	.459	..	6.5	.361	..	3.7	0.252	250 c.c.	0.9	.096
..	9.2	.455	..	6.4	.358	..	3.6	0.247	..	0.8	.080
..	9.1	.452	..	6.3	.354	..	3.5	0.242	..	0.7	.070
..	9.0	.448	..	6.2	.351	..	3.4	0.236	..	0.6	.060
..	8.9	.445	..	6.1	.348	..	3.3	0.231	500 c.c.	0.5	.050
..	8.8	.441	..	6.0	.345	..	3.2	0.226	..	0.4	.040
..	8.7	.438	..	5.9	.341	..	3.1	0.221	..	0.3	.030
..	8.6	.434	..	5.8	.337	..	3.0	0.216	1000 c.c.	0.2	.020
..	8.5	.431	..	5.7	.333	..	2.9	0.211	..	0.1	.010
..	8.4	.428	..	5.6	.330	..	2.8	0.205	..	0.09	.009
..	8.3	.424	..	5.5	.326	..	2.7	0.200	..	0.08	.008
..	8.2	.421	..	5.4	.322	..	2.6	0.195	..	0.07	.007
..	8.1	.417	..	5.3	.318	..	2.5	0.190	..	0.06	.006
..	8.0	.414	..	5.2	.314	..	2.4	0.184	..	0.05	.005
..	7.9	.410	..	5.1	.310	..	2.3	0.179	..	0.04	.004
..	7.8	.407	..	5.0	.306	..	2.2	0.174	..	0.03	.003
..	7.7	.403	..	4.9	.302	..	2.1	0.169	..	0.02	.002
..	7.6	.400	..	4.8	.298	..	2.0	0.164	..	0.01	.001
..	7.5	.396	..	4.7	.294	..	1.9	0.158	..	..	..
..	7.4	.393	..	4.6	.291	..	1.8	0.153	..	..	..
..	7.3	.389	..	4.5	.287	..	1.7	0.148	..	..	..

The appropriate deduction for ammoniacal nitrogen having been made from the total nitrogen obtained by combustion, the remaining weights of carbon and nitrogen still require correction for minute quantities of these elements adventitiously introduced during the analysis. It is desirable that each analyst should make several blank experiments, to determine these coefficients of correction; evaporating a litre of *pure* water with the usual quantities of sulphurous acid and ferric chloride, adding 0.1 gramme of freshly ignited sodic chloride to form a tangible residue. The residue must be burnt and analysed in the usual way. As the result of numerous fairly concordant experiments made in my laboratory, the adventitious C and N introduced into the analytical results, obtained from one litre of water, are 0.00005 gramme of C and 0.00005 gramme of N.

The following data show the delicacy and accuracy of carbon and nitrogen determinations made in this way:—



To 100,000 parts of a sample of water, rendered as nearly chemically pure as possible, 1·5572 parts of sulphate of quinine were added. The following data compare the quantities of organic carbon and organic nitrogen thus actually added to the water, with those afterwards found in two analyses:—

	Present.	Found.	
		I.	II.
Organic carbon in 100,000 parts of water..	0·857 part	0·912	0·904
Organic nitrogen in ditto.....	0·100 „	0·0996	0·098

To 100,000 parts of a similar sample of water, 0·7786 part of sulphate of quinine was added, and the following results obtained on analysis:—

	Present.	Found.		
		I.	II.	III.
Organic carbon in 100,000 parts of water .....	0·429 part	0·435	0·442	0·440
Organic nitrogen in ditto..	0·050 „	0·047	0·048	0·048

To 100,000 parts of a third similar sample of pure water, 0·07786 part of sulphate of quinine was added. On analysis this water yielded the following numbers:—

	Present.	Found.		
		I.	II.	III.
Organic carbon in 100,000 parts of water.....	0·043 part	0·047	0·050	0·055
Organic nitrogen in ditto..	0·005 „	0·006	0·005	0·006

The close approximation of the experimental to the calculated numbers is the more striking when it is remembered that the weight of nitrogen *actually determined* in the litre of water used for analysis was, in the last series, only 0·00005 gramme—a quantity which if converted into platinum salt would only weigh  $\frac{8}{10}$ ths of a milligramme.

Applied to actual specimens of potable water the accuracy of the method can be tested by the uniformity of results obtained in duplicate analyses of the same samples of water. The following instances will suffice to illustrate this point:—

Results of analysis expressed in parts per 100,000.			
		I.	II.
Thames water as supplied {	Organic carbon ....	0·280	0·285
to London .....	„ nitrogen ..	0·032	0·035
River Lee water as supplied {	Organic carbon ....	0·231	0·239
to London .....	„ nitrogen ..	0·042	0·042
Kent Company's water as {	Organic carbon ....	0·054	0·056
delivered in London ..	„ nitrogen ..	0·016	0·017

But, as practical illustrations of the trustworthiness of the process, these examples, if multiplied a hundred fold, could scarcely afford such satisfactory evidence as that presented by the results of the monthly analyses of the water delivered by the eight metropolitan companies, made for the Registrar General during six years, and exhibited in the accompanying diagrams.

Diagram No. 1. shows the mean proportions of organic elements (organic carbon and organic nitrogen) in the waters from the Thames and Lee, and compares them with that found in the deep well water of the Kent Company, from 1868 to 1873 inclusive. It also shows, in five-day averages, the rate of flow of the Thames at Long Ditton nearly opposite Hampton Court Palace, and consequently near the place where the Thames Water Companies abstract their supplies. This last information is plotted from daily gaugings furnished to the Rivers Commission in 1874, by Mr. John Taylor, C.E.—the engineer to the Lambeth Water Company.\*

Unfortunately no similar gaugings have been executed on the River Lee, but probably the rainfall and its effect upon the river flow are not very different in the two basins.

The Thames is almost invariably more polluted by organic matter than the Lee, whilst the water raised from deep wells in the chalk by the Kent Company is much purer than either, as far as organic matter is concerned.

The diagram shows how sharply the distinction between these three waters is drawn by the analytical determinations of organic carbon and nitrogen. In no instance does the curve representing the average organic impurity in the Thames approach near to that indicating the like impurity in the deep well water, whilst the curve of organic contamination in the Lee water intersects the Thames curve but twice, and the deep well curve only once in six years. Even these intersections are interesting as illustrations of the delicacy of the analytical method. That of the Lee and deep well curves occurred at a time when, through the defective storage arrangements of the Kent Company, the deep well water was subjected to slight pollution from surface soakage. In April, 1868, I inspected the works and pointed out the defect to the late Mr. Morris, the engineer to the Company. No intersection has since occurred.

The passage of the Lee through the Thames curve occurred very slightly in February, 1870, and again more decidedly in February, 1873, on both occasions after heavy floods. We have not to seek far for the cause of these exceptional intersections. At those dates, four out of the five Thames Companies supplied from hand to mouth—they had no storage, and consequently though obliged to supply highly

\* See 6th Report of the Rivers Commission, 1874, p. 474.

polluted water during floods, they instantly derived the advantage of a purer stream when the floods subsided. Thus the Thames water delivered in January, 1873, when the river was conveying 4,200 millions of gallons daily, contained nearly twice as much organic matter as it did in the following month, when the flow of the river was only 1,700 millions of gallons per day. On the other hand, vast volumes of the polluted water of the Lee had been stored by the East London Company during the heavy floods which prevailed from the beginning of December, 1872, to the end of January, 1873. The whole of this polluted water had not been distributed before the collection of the sample on the 10th of February, and thus the organic impurity in this flood water of the Lee exceeded in amount that present on the same date in the fair-weather water of the Thames.

The diagram also shows how faithfully the analytical results record the variations in the three great conditions which govern the intensity of organic contamination in river waters, viz.:—(1.) Heavy floods. (2.) Small floods when the river is low; and (3.) Decay of vegetation in autumn.

The effect of heavy floods in enormously increasing the pollution of the Thames is strikingly seen throughout the diagram, but it is especially exemplified by the abrupt rise of the Thames curve in the months of January, February and December, 1869; in January, 1870; in January, April, November and December, 1872; and in January and March, 1873. Reference to the Lee curve shows that the organic matter in that river is simultaneously affected, but, as a rule, to a less violent extent.

Not only do heavy floods bring down the Thames a vast aggregate, and much increased proportional, quantity of filthy organic matter, but in dry weather a thunder shower, for instance, will sometimes wash into the river or its tributaries the polluting matters that have been accumulating for weeks in stagnant ditches and cesspools, and this without increasing the flow of the river to any great extent. In this way, a very small flood upon a low river will sometimes impart to the water a greatly increased proportion of organic impurity. In October, 1869, and November, 1873, the analytical curve of the Thames shows that the foulness of the water was markedly increased by such small floods. In the Lee this effect of small floods is much less conspicuous owing to the large storage reservoirs of the East London and New River Companies.

The plotting of these curves has also brought out the interesting fact, that the quality of the deep well water delivered by the Kent Company is not entirely, though it is nearly, unaffected by heavy rain. In the years 1868 and 1869, the apex of the deep well curve coincides with those of the Thames and Lee too frequently to be the result of accident. Whether this arose from the actual direct access of a small

proportion of surface water to the wells, or from an acceleration of the process of natural filtration by surface pressure, cannot now be determined; but previous to the year 1872, part of the water was pumped into an uncovered reservoir, and was there liable to some amount of pollution. Since the covering and cementing of the reservoir, this effect has been barely if at all perceptible.

Independently of floods, the decay of vegetation late in autumn must obviously produce a decided deterioration in the quality of river waters; but as this decay often takes place simultaneously with the occurrence of floods, it is not often possible to isolate its effects. In October, 1868, and November, 1870, however, the Thames was low, and the separate result of decaying vegetable matter is clearly indicated by the abrupt rise of the analytical curve. A small flood at this time of the year or soon after the "fall of the leaf," produces an enormous effect upon the quality of the water; thus late in November, 1869, a rise of the river from 500 millions of gallons to 930 millions of gallons daily flow, increased the organic impurity by 57 per cent.; between September and the 10th of October, 1871, a rise from 450 millions of gallons to 840 millions of gallons, which last number represents about the average flow of the Thames, to more than three times its previous amount; whilst in November, 1873, an increase of daily flow by only 330 millions of gallons augmented the organic impurities to double their previous amount.

The translation, into analytical numbers, of the effects of the chief conditions which determine the quality of the water derived from the Thames, the Lee, and the deep wells sunk into the chalk, is most clearly seen in diagram No. 1, in which each kind of water is represented by a single curve; but it is also interesting to see how far the more minute differences of treatment which the three kinds of water receive at the hands of the eight London water companies are expressed in the determinations of organic carbon and nitrogen. For this purpose it is necessary to plot out a more elaborate diagram (No. 2), in which the results of analysis yielded by each Company's water are represented by a separate curve.

As the water from deep wells is delivered by only one company, the same curve represents this kind of water in both diagrams; but the water of the Lee is distributed by two, and that of the Thames by no less than five distinct companies; and, as the water of each company is submitted to monthly analysis, it follows that the average curve of the Lee must be resolved into two, and that of the Thames into five constituents. This decomposition of the river water curves distinguishes diagram No. 2 from diagram No. 1. In all other respects they are identical. The more elaborate diagram serves to illustrate the following points:—

1. *The difference, in regard to Organic Impurity, of the Water dis-*

*tributed from the Lee by the New River and East London Companies.*—The New River Company abstracts the chief portion of its supply from the Lee at a point above the outfall of the Hertford sewage, and where in dry weather it consists almost entirely of spring water. They mix it with about one-fourth of its volume of spring water, and occasionally, though rarely, with a small proportion of water pumped from deep wells; but the volume of water, other than Lee water, distributed by this Company is too small to affect materially the composition of the water delivered to their customers in London, although all these subsidiary supplies tend to improve the quality of the water.

The East London Company abstract their supply at Ponder's End, 14 miles lower down the river, and after the accession of much impurity which reaches the Lee below the intake of the New River Company. On the other hand, the East London Company possess much greater storage capacity in their reservoirs, which enables them to close their intake during short floods, although they are obliged to take in water during long continued rainy weather.

The analytical curves clearly express these differences in the conditions under which the two Companies work. The New River curve is generally below that of the East London water, and, with one or two notable exceptions, it crosses the latter only in very dry weather, when much of the filth, which otherwise finds its way into the Lee, is retained by an absorbent soil; and thus the river maintains a chemical character approaching to that of spring water, even down to the intake of the East London Company. The notable exceptions illustrate the effect of large storage capacity upon the chemical quality of the water sent out to consumers. Thus between the collection of the samples in January and February, 1869, there occurred two heavy floods with an interval of fifteen days of good water between them. By taking advantage of their great storage capacity, the East London Company rejected some of the bad water, and supplied in February a beverage of superior quality to that distributed by the New River Company, which has barely five days' storage room. A similar instance occurred in April, 1872, and another in March, 1873.

On the other hand, during the continuance of the imperfections in the Kent Company's works, the New River curve occasionally intersected that representing the organic impurity of the former Company's water, but this has never occurred since the year 1870.

2. *The Difference, in regard to Organic Impurity, of the Water distributed from the Thames by the five Companies drawing from that River.*—Of these five Companies the West Middlesex is distinguished for the comparatively large capacity of its storage and subsidence reservoirs, and for the perfection of its filtering plant. During the last eight years this Company has never sent out water which was in

the slightest degree turbid. Though water is drawn from the river every day, whatever its state may be, in times of exceptionally foul water the intake is reduced as much as possible. The Company has storage for about seven days' supply. These conditions under which the West Middlesex Company works are faithfully recorded in the results of the analytical examination of the water. Thus the curve representing the proportion of organic elements sent out by this Company is in times of flood always much lower than that of any other Thames supply; as is strikingly seen by a comparison of the curves in January, February, and December, 1869, January, 1870, February and October, 1871, January, April, November, and December, 1872, and January, March, and November, 1873.

But the West Middlesex Company cannot always avoid admitting flood water into its reservoirs, and when once let in, this water can only be again discharged by the distributory mains. It mixes with and depreciates the quality of the fair weather water which comes in after the subsidence of the floods. In fact the storage of river water, unless the reservoirs possess a much greater capacity than those of any of the Metropolitan Companies, is not an unmixed good; because the stored water is liable at times to be more polluted than that flowing in the adjacent river. The injurious effect of the West Middlesex storage reservoirs is exemplified by the curve representing organic impurity in June, 1869. In the preceding month samples of the fine-weather Thames waters were collected at the commencement of a flood, and all, except the West Middlesex, were much polluted. In the following month, however, the samples were collected from a low river several days after the subsidence of a series of freshets. The West Middlesex Company was still distributing the flood water which it had impounded during the previous thirty days, whilst the remaining four Thames Companies were drawing from a comparatively pure river. Thus these last Companies distributed much better water in June than in May, whilst that sent out by the West Middlesex continually deteriorated from April to June. The same effect of greater storage capacity again receives its analytical illustration in February and March, 1870, November, 1871, and February, 1872.

Of the remaining Companies drawing from the Thames, the Lambeth and Chelsea alone abstract at a point below the junction of the Mole with the Thames. Partly on this account, but chiefly by reason of their inferior subsidence and filtration plant—the Chelsea Company has no subsidence reservoirs, and the muddy river water runs directly on to their filter-beds—the water delivered by these Companies might be expected to be of inferior quality. An inspection of diagram No. 2 shows that the summits of the curves are generally capped by the representatives of these waters. This is conspicuously the case in

January, 1868, December, 1869, January and November, 1870, February, 1871, January, April, November, and December, 1872, and January, March, August, and November, 1873. The inferiority of these waters would be still more conspicuous were it not for the erratic movements of the Southwark curve. The Southwark Company's district grows more rapidly than that of any other Metropolitan Water Company. In January, 1868, it supplied only 14 millions of gallons daily, whilst in November, 1873, the daily delivery had increased to  $19\frac{1}{2}$  millions of gallons. This is an inconvenient rate of increase. The Company have from time to time made great efforts to keep pace with it, in the subsidence and filtration plant; and the curve of organic impurity represents the spasmodic struggles of Mr. Quick, the Company's engineer, in this contest with dirty water. In January and February, 1869, he was hopelessly beaten; in May and October of the same year the curve again reaches the summits of the peaks, and not until December can the Company stand the flood test. Then, however, there is considerable improvement until April, May, and June, 1871, when the demands of a thirsty population again demonstrate the insufficiency of the enlarged plant. Once more, however, vigorous efforts are made, and throughout the rest of that and the two following years the Company delivers water of medium quality.

3. *The Influence of the Date of Collection upon the Quality of the Sample.*—As a rule, all the samples of river water are collected on the same day of the month, but occasionally, owing to a failure in the stand-pipe from which the water is drawn direct from the main, the collection is delayed for a few days. Now if a flood occurs on the date of collection of the second sample, or on the previous day, that sample ought to be more highly polluted with organic matter. A case of this kind occurred in March, 1870. All the samples of Thames water, except that from the Chelsea Company's mains, were collected on the 2nd of the month, just before the occurrence of a heavy flood on the 6th,\* which increased the volume of the river to 2,000 millions of gallons. The Chelsea sample was collected on the day after the flood, and the analytical curve shows how much more highly it was polluted by organic matter.

*Not only, therefore, does this process for the determination of organic elements clearly define the broad differences between deep-well, Lee, and Thames water, but it has also shown itself competent to reveal the finer shades of quality in waters drawn simultaneously from the same source, but treated differently by the various Companies who manipulate them.*

Against these advantages it must be acknowledged that the process involves more trouble and more careful manipulation than are usually

\* These floods on single days are shown in the diagrams by blue lines rising from the curve, which represents the average flow of the Thames in periods of five days each.



bestowed upon what are called "commercial" analyses. Now although these drawbacks ought not to be paramount considerations where such important issues are involved, yet if any other more simple method existed by which trustworthy quantitative information about the organic matter in water could be obtained, the process which I have been describing would cease to have a *raison d'être*. I showed eight years ago, and my proofs have never been called in question, that the incineration and permanganate processes are quite useless; nevertheless the latter is still used by Dr. Letheby in his monthly reports to Medical Officers of Health. But there still remains the albuminoid-ammonia method of determining organic nitrogen. I need not describe this method, as it is well known, and is now almost as generally used by analytical chemists as were formerly the incineration and permanganate processes. This method depends upon the fact that by boiling with an alkaline solution of potassic permanganate, most nitrogenous organic bodies are decomposed with evolution of ammonia. But the total nitrogen contained in the organic bodies is rarely evolved as ammonia, and the proportion so evolved varies very widely when different kinds of organic matter are submitted to this reaction. The authors of the process indeed soon withdrew their statement, that albumin yielded all its nitrogen as ammonia by ebullition, first with potash and then with alkaline solution of potassic permanganate (*Journal of Chem. Soc.*, xx, 593), nevertheless the results yielded by this method continue to be entered in analytical tables as organic nitrogen, although its authors have never sanctioned such an interpretation.

An examination of this method must convince all that it is incapable of converting into ammonia either the whole or any definite proportion of the organic nitrogen of potable waters. The results obtained by the authors themselves, when they operated upon known quantities of organic matter, prove this most conclusively: as is seen from the following comparison of their experimental numbers with those calculated from the formulæ of the bodies operated upon. 100 parts of each substance yielded:—

	Nitrogen actually present.	Nitrogen found.
Asparagine .....	18·66	18·05
Piperine .....	4·91	4·45
Diamylamine chloride .....	7·24	6·53
Amylamine .....	16·09	17·96
Diphenyl tartramide .....	9·33	8·41
Gelatin.....	18·30	10·46
Casein .....	13·0 to 16·0	6·26
Albumin .....	13·0 to 16·0	8·24

	Nitrogen actually present.	Nitrogen found.
Morphine.....	4·91	2·31
Codeine .....	4·42	2·47
Papaverine .....	4·12	1·81
Strychnine .....	8·38	4·49
Iodide of methyl-strychnine..	5·88	2·74
Brucine .....	7·11	3·79
Quinine sulphate .....	7·51	3·71
Cinchonine sulphate .....	7·84	{ 4·70 4·45
Nicotine .....	17·28	8·89
Naphthylamine .....	9·80	{ 5·48 5·61
Toluidine.....	13·09	{ 7·27 6·83
Rosaniline acetate .....	11·63	{ 5·25 5·34
Creatine .....	32·07	10·38
Theine .....	28·86	7·03
Uric acid.....	33·33	5·76
Urea.....	46·66	0·00
Picric acid .....	18·34	0·00

Thus out of 25 nitrogenous organic substances experimented upon, only 5 yielded, approximately, the whole of their nitrogen as ammonia, when treated by the albuminoid-ammonia process. Of the remainder, some evolved one-half, others one-third, one-fourth, or even none of their nitrogen as ammonia. To this list may be added the results obtained by Dr. Armstrong and myself on submitting various nitrogenous organic matters to the albuminoid-ammonia process (*Jour. Chem. Soc.*, vol. xxi, 1868, p. 98). We found that strychnine, when treated as directed by the authors, yielded rather more than one-third of its nitrogen as albuminoid-ammonia, narcotine between one-third and one-half, quinine sulphate about one-half, and soluble peaty matter a proportion varying from less than one-third up to nearly one-half. Out of the substances of known composition which have thus been experimented upon, the following may be selected as of peculiar importance, because they are liable to be present in potable water:—Gelatin, casein, albumin, creatine, uric acid, and urea;—and it will be seen on reference to the foregoing analytical results, that these substances yield up, when treated by the albuminoid-ammonia process, proportions of their nitrogen varying from more than one-half down to nothing. The total immunity of urea from the reaction is peculiarly unfortunate, because it is prac-

tically impossible to estimate the urea, in a good potable water to which fresh urine has been added, by boiling with sodic carbonate; and yet the estimation of the nitrogen of urea, not to speak of its carbon, is of the utmost importance in the investigation of waters polluted by sewage. On the other hand, peaty matter, the presence of which in water is of comparatively little importance, yields up a large proportion of its nitrogen as albuminoid-ammonia. It is, therefore, evident that this process can give no evidence whatever touching the proportion of organic matter present in potable water, whilst it is equally evident that it cannot even indicate the relative quantities of organic nitrogen in different samples, unless the proximate constituents of the organic matter happen to be of the same kind, and in the same relative proportions in the samples compared—a coincidence which must obviously seldom or never occur. Neither can the albuminoid-ammonia process be used to indicate, either the presence, or the proportion of *albuminoid* as distinguished from other nitrogenous organic compounds. This conclusion is not only rendered unavoidable by the experiments recorded above, but it is also established by the fact that peaty matter, either alone or as it occurs in water, yields abundance of so-called albuminoid-ammonia, although the existence of protein compounds—so prone to change—in a material which has been exposed to air and moisture for thousands of years, is clearly an untenable assumption.

It is, therefore, not surprising to find that the application of this process, both to natural and artificially prepared waters, discloses wide discrepancies and great irregularities in the evolution of albuminoid-ammonia, that is in the estimation of organic nitrogen. The following examples, in which the nitrogen obtained as albuminoid-ammonia is contrasted with that actually extracted from the waters by the combustion process, serve to show how the irregularities observed, in the case of nitrogenous organic compounds of known composition, are reproduced, when the, for the most part, unknown nitrogenous compounds in potable waters are similarly treated.

Results of analysis expressed in parts per 100,000 :—

*Artificial Waters containing Peaty Matter.*

	Organic nitrogen by combustion.	Organic nitrogen by albuminoid-ammonia process.
I. ....	·068 part	·016 part.
II. ....	·042 „	·016 „
III. ....	·076 „	·022 „
IV. ....	1·015 „	·308 „
V. ....	1·175 „	·422 „
VI. ....	·029 „	·011 „

*Natural Waters.*

	Organic nitrogen by combustion.	Organic nitrogen by albuminoid-ammonia process.
Chelsea Company's water, January, 1868 .....	·058 part.	·011 part.
West Middlesex, ditto, ditto....	·027 „	·012 „
Southwark, ditto, ditto .....	·061 „	·024 „
Grand Junction, ditto, ditto ....	·031 „	·006 „
Lambeth, ditto, ditto .....	·062 „	·030 „
Artesian Well Water, October, 1874 .....	·033 „ }	{ ·003 „
Artesian Well Water, April, 1876 .....	·032 „ }	{ ·004 „
Sea-water (Sample No. 1).....	·217 „	·006 „
„ (Sample No. 2).....	·134 „	·018 „

It is almost superfluous to say that any opinion based upon the proportion of albuminoid-ammonia obtainable from a sample of potable water must almost necessarily be erroneous, like that to which the authors of the process themselves were led, when they declared the water of Bala Lake, and that supplied to Manchester from the Derbyshire hills, to be more polluted than Thames water. In the course of my work upon the Rivers Commission, I have again and again met with such errors of judgment, into which chemists using this process have been led. It would be preferable to depend upon chlorides and nitrates alone, rather than upon a method of estimation, the results of which do not admit of interpretation.

The numerous experiments, on this process, made by others as well as by myself, have led me to the following conclusions:—

1. That the albuminoid-ammonia process affords no evidence whatever of the absolute quantity, either of organic matter or of organic nitrogen, present in potable water.

2. That it does not indicate, even approximately, the relative quantities either of organic matter or of organic nitrogen in different samples of such water.

3. That it affords no indication either of the presence or of the proportion of *albuminoid* as distinguished from other nitrogenous organic compounds.

4. That it is therefore entirely useless in the examination of waters for sanitary purposes.

In conclusion, I claim for the combustion process, after nearly nine years' experience of it:—

1. That it is the only method at present known which affords any trustworthy information respecting the organic matters present in potable waters.

2. That it is the only method which even professes to determine organic carbon in such waters.

3. That the determinations by it of organic carbon and nitrogen are fairly accurate, notwithstanding the very minute quantities of matter dealt with ; and that the errors, even of a comparatively inexperienced analyst, are far within the limits which would affect a verdict upon the quality of the water submitted to investigation.

4. That it is the only process which discloses the proportion of nitrogen to carbon in the organic matter of waters, such information being often of prime importance in reference to the origin of the organic matter.

5. That since the modifications which have been made in the mode of evaporation, the process can now be conducted in any laboratory and with a moderate expenditure of time and labour.

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