

AMERICAN RESEARCHES ON
WATER-ANALYSIS

AT the instance of the U.S. National Board of Health, a comprehensive investigation relating to analysis of water has been recently conducted by Prof. J. W. Mallet, F.R.S., of Virginia, assisted by several chemists and others. It was proposed to examine carefully the chief processes in use for chemically determining the organic matter or its constituents, in drinking water, to test the absolute and relative accuracy of the results these processes are capable of yielding, and, as far as possible, to ascertain the nature and scope of the practical conclusions available for sanitary purposes, which might thence be secured.

A preliminary report of this inquiry has appeared in a recent supplement (No. 19) of the National Board of Health *Bulletin*, and we propose here to give our readers some idea of the nature of it.

Three chemists took charge severally of the so-called "combustion process" of Frankland and Armstrong, the "albuminoid ammonia process" of Wanklyn, Chapman and Smith, and the permanganate process as advocated by Tidy; they were, Mr. W. A. Noyes, who worked at Baltimore, Dr. Ch. Smart, U.S.A., at Washington, and Dr. J. A. Tanner, U.S.N., at Virginia. The water-samples were collected and distributed to these three places by Prof. Mallet, and all three chemists were required to examine their several samples on the same day. Prof. H. Newell Martin undertook a simultaneous microscopic examination, and pathological observations on the effect of injecting the waters, concentrated by evaporation at a very low temperature, under the skin of rabbits.

After a large amount of preliminary and special work, nine classes of waters were obtained or prepared, for the main series of test analyses, as follows:—

Class I.—Natural waters, believed to be wholesome (including the water-supply of some of the principal cities).

Class II.—Natural waters which were believed to have actually caused disease in those who drank them.

Class III.—Natural waters of doubtful, but more or less suspected character.

Class IV.—Artificially prepared waters, made by adding to wholesome water, certain amounts of various infusions of *vegetable* organic matter, such as drinking water is liable to be contaminated with.

Class V.—Waters prepared with various forms of *vegetable* refuse, from manufacturing or industrial operations.

Class VI.—Waters prepared with *animal* (or partly animal) organic matter of natural origin.

Class VII.—Water prepared with *animal* refuse from manufacturing or industrial operations.

Class VIII.—Water prepared by adding morbid products of human disease.

Class IX.—Solutions, in distilled water, of carefully determined amounts of pure substances of definite chemical composition.

The report first deals with the *degree of accuracy* of the three processes examined, a matter which may be looked at in two ways: first, as to the concordance of the results of each process in duplicate or triplicate experiments on the same water; and secondly, as to the agreement of the results with the actual, quantitatively known, contents of a particular water.

In the case of multiplied experiments on the same water, then, the author first shows in three successive tables (for the three processes), the divergence of individual results from the mean, as *percentage on the mean*. It appears that, on the whole, the most closely concordant results were furnished by the permanganate process, and the least so by the combustion process, the albuminoid-ammonia process holding the intermediate position.

Next, a table is given showing the extent of agreement of results obtained by the different processes with quantities of organic constituents known to be actually present. The figures strikingly indicate certain important defects of the several processes, though (it is pointed out) they must be looked at in a broad, general way, remembering the small number of organic substances treated and their special characters.

The Report proceeds to deal with the effects on the results by the different processes of varying the extent of dilution of the same organic substances in water. Here, as regards the combustion process, distinct confirmation is had of the existence of

two forms of constant error affecting evaporation. The weaker the solution the less is the amount of organic carbon obtained, and the larger the figure for organic nitrogen. If the usual interpretation of Frankland's C : N ratio be applied, the curious and important result of these sources of error follows, that the more dilute an organically-polluted water is, the more animal-like in origin will its polluting material seem to be; while the stronger it is, the greater will be the tendency to refer the contamination to a vegetable source—a distortion of conclusions manifestly in the opposite direction to that commonly assumed to be safe.

As to the albuminoid ammonia process, the weaker the solutions, the higher are the results obtained, both for free and albuminoid ammonia, the influence common to both being probably that of imperfect condensation in the distillation having a less effect as the quantity of ammonia is stronger. The lower results from the stronger solutions for albuminoid ammonia, may be partly due to the fixed charge of alkaline permanganate to the quantity of organic matter to be acted upon.

The results of the permanganate process are shown to be much less influenced by varying dilution within the limits of those experiments than those of the other processes.

The following, briefly stated, are the author's

Special Conclusions as to the Combustion Process

1. The combustion itself, carried out according to Frankland's directions, is a process of great delicacy, and quite satisfactory in its details, with proper precautions, and in trained hands. Gaseous volumetric analysis with the aid of the Sprengel vacuum, is sufficient.

2. The Frankland process is quite within reach of the manipulative skill of any fairly-trained chemist, but it requires practice and probably pretty constant practice. It is better adapted for large public laboratories, where many samples of water are examined, than for occasional use by a private individual.

3. The defective point is the failure of the evaporation to leave a residue representing the original organic matter; this (suspected hitherto) is regarded as now established. There are two constantly present errors (greatest with little organic matter), viz., loss of carbon, and gain of nitrogen from the atmosphere, the latter probably partly balanced by loss of that originally present in the water.

4. These errors, affecting unequally the carbon and nitrogen, are liable to alter the statement of the C : N ratio, and so distort sanitary conclusions.

5. The result for organic nitrogen, by the combustion process, is also affected indirectly by the errors connected with determination of the ammonia ("free ammonia"), as the nitrogen belonging to this has to be subtracted from the gross result.

6. A further, indirectly operative, cause of error as to the nitrogen arises from the varying loss of ammonia by dissociation of its salts during evaporation. The time occupied in evaporation, as well as the amount of ammoniacal salts present, will influence the amount of loss. Such error will mostly be very small, but may affect considerably the result for *organic* nitrogen.

7. The presence of nitrates presents a special difficulty in the combustion method. Mr. W. Williams's application of the copper-zinc couple deserves more precise quantitative examination than it has yet had. The simultaneous presence of urea with nitrites and nitrates, presents a case of peculiar difficulty, with several sources of error.

8. The formation of sulphuric acid during evaporation with sulphurous acid seems to occur oftener than has been recognised. It is much to be deprecated, though its effect, at any rate on the carbon determinations, has not seemed so great as might have been expected.

9. The combustion process, in its present form, cannot be considered as determining the carbon and nitrogen in a sense to justify the claim of "absolute" value for its results, which has been denied to those of other methods. It is but a method of approximation, involving sundry errors, and in part, a balance of errors.

10. There is, however, good ground for believing, that in many, perhaps most cases, its results for organic carbon may, with proper precautions, be made more valuable than the indications of the permanganate process, and its results for organic nitrogen more valuable than the indications of the albuminoid ammonia process.

Special conclusions as to the Albuminoid-ammonia Process

1. In the determination of both "free" and "albuminoid" ammonia there is a loss, which may be quite considerable, from imperfect condensation of the ammonia during distillation. This varies especially with the efficiency of the cooling apparatus and the time occupied.

2. Where waters contain urea and other amidated bodies, such as the leucine and tyrosine of putrefactive decay, some ammonia is so easily formed from these substances by boiling with sodium carbonate, or even without this addition, that it is impossible to distinguish sharply between pre-existing "free" ammonia (of ammoniacal salts), and that formed by the action of alkaline permanganate, the so-called "albuminoid" ammonia. This source of error as to free ammonia reacts (as noticed above), on the result for organic nitrogen by the combustion process.

3. There is no satisfactory evidence for Wanklyn's view, that, in distilling with alkaline permanganate, definite and simple fractions of the nitrogen of organic matter are given off as "albuminoid" ammonia. Such results may be varied at pleasure for most substances, by modifying the conditions of distillation.

4. If the distillation with alkaline permanganate be carried out according to Wanklyn, the nitrogenous organic matter is often so gradually acted upon, as to make the ending of the process indefinite; ammonia is still coming off when the distillation has to be stopped, the contents of the retort being nearly dry. Here an unknown fraction of the possible amount of albuminoid ammonia fails to be collected, and is but vaguely indicated by + after the figures recorded.

5. There is evidence that in some cases nitrogenous matter is volatilised during the distillation for free ammonia, which, if it had been retained, would have yielded up its nitrogen as albuminoid ammonia. Not affecting the Nessler reagent, such matter escapes detection.

6. The albuminoid-ammonia process proper, *i.e.* distillation with alkaline permanganate and determination of the ammonia evolved, is admittedly simple, and easily carried out with very little preparatory training.

7. The value of the results by this process depends more on watching the *progress* and *rate* of evolution of the ammonia than upon determining its total amount.

8. The recorded results by this process show a good deal of similarity between the figures for albuminoid ammonia and those for organic nitrogen (by the combustion process), but with frequent discrepancies of varying extent, such as prevent the one being taken as the accurate measure of the other.

Special Conclusions as to the Permanganate Process

1. The results by the Tidy method (the acidified permanganate at common temperature) and that of Kubel (operating at boiling point) differ irregularly from each other, the latter usually giving much higher figures, as was to be expected, but the ratio between the results by the two methods varies much in different cases.

2. On the whole, there seems to be a nearer approach to proportionality with the quantities of organic carbon found by the combustion process on the part of the Kubel process than on that of the Tidy process, but to this there are some very notable exceptions.

3. In a good many cases, the Kubel results are, contrary to the general rule, lower than those by the Tidy method. This seems to be due to loss of organic matter by volatilisation with the escaping steam from the boiling liquid before time has been afforded for action on the permanganate. Of course, a similar loss may have occurred in other cases, but not to the extent of reversing the general rule; and this may in part explain the absence of any uniform ratio between the figures yielded by the two methods.

4. The results by the Tidy process are liable to variation with the atmospheric temperature at the time of operation.

5. The amount of oxygen consumed by a specimen of water is probably in all ordinary cases much below that required for complete oxidation of the organic matter present, and does not stand in any fixed ratio thereto; it cannot be taken either as a measure of the organic carbon or of the total organic matter. Still a distinct general resemblance may be traced between strongly marked results, high or low as the case may be, for the consumption of oxygen on the one hand, and organic carbon (by the combustion process) on the other, and closer agreement is observable regarding waters of generally similar character.

6. The permanganate process is capable of giving more valu-

able information in regard to a water by watching the *progress* and *rate* of the oxidation of organic matter present than by any single determination of the actual amount of oxygen consumed in a given time.

7. For such observation of the progress of oxidation, the two determinations prescribed by Tidy, *viz.* of oxygen consumed in one hour and three hours respectively, are not sufficient, nor is the latter period of three hours long enough to indicate the general behaviour of the water with the acid permanganate.

As to other chemical determinations, the discrepancies in those of total solids left on evaporation, of the loss on ignition of this solid residue, and even of chlorine, are noted as illustrating the comparative roughness of the methods with which those results were obtained when very small quantities have to be dealt with. A coincidence is often presented between alkaline reaction of a water and the occurrence of nitrites and nitrates in considerable quantity, suggesting a recollection of the conditions under which nitrates are produced on a large scale in the decay of nitrogenous organic matter. Those salts, however, also occur pretty largely in some cases without alkaline reaction, and in other cases there was alkaline reaction and also much nitrogenous matter, but no nitrites nor nitrates. Ammonium nitrates seem to be rare, the basis-constituent being rather mostly non-volatile—no doubt calcium, magnesium, or one of the alkaline metals; this is noticed as in relation to possible reduction to nitrite, and consequent loss of nitrogen in the combustion process. Experiments with tannin showed the utter worthlessness of this group-reagent of Kämmerer for the purpose for which he has advocated its use. The general series of analyses of dissolved gases illustrate how the results are influenced by varying conditions of oxidisability of organic matter present, temperature, extent of exposure to the atmosphere, and interchange with it, in both direction, of gaseous constituents.

With regard to the *microscopic and pathological results*, Prof. Mallet, feeling himself incompetent to properly discuss these, prefers leaving them to speak for themselves, and merely remarks on some of the difficulties of such research, and, at the same time, on its importance and value when rightly conducted.

Passing now to sanitary conclusions and interpretation of results, the Report deals with

Chemical and Biological Results as contrasted with the actual Sanitary History of the Natural Waters Examined

Now on inspection of the tabulated results it appears that *no strongly marked generic difference is presented by the results from any of the processes for estimation of organic matter or its elements between the generally wholesome waters of Class I, and the waters of Class II, medically condemned and fairly assumed as pernicious.* This applies equally to the highest, the lowest, and the average results. No one could, with those figures to guide him, refer a water of unknown origin to one or other of the two classes, on the basis of chemical analysis by any or all of the three methods. Attention is called to the smallness of the amount of organic matter indicated as present in many of the most dangerous waters, giving important evidence against any chemical theory of the production of disease from this source (on the simple assumption that some of the chemical products of decomposition of organic matter are poisonous or noxious in their effect on the human system). Thus in the case of two waters of highly dangerous character, if the whole of the organic carbon and nitrogen present existed as strychnine, it would be necessary to drink about half a gallon of the water at once, in order to swallow an average *medicinal* dose of the alkaloid. It is not easy to believe that the ptomaines, or other chemical products of putrefactive change, can be so much more poisonous than the strongest of recognised poisons. While most of the mischief in drinking water is probably attributable to living organisms, the possibility is noted, that indirectly a large amount of organic matter in water may be more dangerous than a smaller quantity, as furnishing on a greater scale the suitable material and conditions for development of organisms. Whether variations in the mere quantity of organic matter within such limits as occur in water likely to be used for drinking are of much importance in this respect, is a question on which (in the author's opinion) depends largely the utility of all attempts to estimate the quantity of organic matter or its constituents as such.

A much more conspicuous difference between the waters of Classes I. and II. is presented by the results for nitrites and nitrates. These salts are either absent or present in but trifling

amount in the wholesome waters of Class I., but almost universally present, and often in large quantity, in the pernicious water of Class II. They are very variable as to presence and amount in the doubtful waters of Class III. This result is worthy of special attention in view of the different opinions which have been expressed (by Wanklyn, Angus Smith, Frankland, Griess, Ekin, Haines, &c.) as to the sanitary conditions of nitrites and nitrates in water.

Among the artificially polluted waters were a number of samples of such general character as to be under the gravest suspicion on sanitary grounds (suspicion corroborated in sundry cases by biological tests), in which, nevertheless, nitrites and nitrates were not found; but these waters had an extraordinarily large amount of organic matter, generally accompanied by very large amounts of ammonia.

Looking at the results for Classes I. and II., and bearing in mind the conclusions reached by Müller, Schloesing, and Muntz, Störer, Warrington, and others, as to the process of nitrification being due to presence of an organised ferment or ferments of bacterial character, "the idea suggests itself whether the noxious character of waters containing largely nitrates and nitrites—themselves presumed to be harmless—and but very little organic matter—which ought to be present, of some sort, to support the 'previous contamination view—may not be in reality due to the presence of a special nitrifying ferment, itself to be classed among the lower organisms capable of propagating disease.'"

Two points are noted as requiring caution in regard to the above conclusions: first, the samples may have undergone some chemical change in the interval from their collection to their reaching the analysts (but such changes could hardly have been great); secondly, it was necessary to take *exaggerated instances* of mischief; and the organic impurities present in the waters concerned may not be the same as those which would produce slighter, but, in time, serious ill effects. Slighter forms of disease, really attributable to drinking water, may perhaps be numerous, and possibly of various types, but generally the difficulty will be too great of securing, in view of the many factors concerned, any satisfactory evidence as to their cause.

In regard to determinations of chlorine, the results are in many cases of water from shallow wells, significant enough of contamination by fluid animal excreta. The amount of chlorine in the case of several wells near the sea, shows the need of thought as to the natural source of a water in drawing conclusions from the presence of chlorides. Even where chlorine has come in with organic matter, this impropriety in too hastily deciding, as is sometimes done, that a small quantity indicates vegetable, and a large quantity animal contamination is illustrated by several cases.

Prof. Martin and Dr. Hartwell were asked to independently mark waters as "dangerous" and "suspicious" on the basis of the biological observations. The results, as summarised in a table, prove that these methods will not afford the means of deciding between a wholesome and an unwholesome natural water. Several of the waters believed to be fairly wholesome, and certainly in use on a large scale, are marked "suspicious," while not one of the waters believed to have proved themselves pernicious when used by man, are set down as "dangerous." In many cases the waters which affected rabbits most, contained *very large* amounts of organic matter, so large as to probably invalidate comparison with natural waters or with the much more dilute specimens of prepared water. On the other hand, with three strengths of a solution of organic material, it was not the strongest that produced the most marked effects. The pernicious character of waters containing relatively but very little organic matter, seemed to be proved by several cases; probably supporting the idea that it is not mainly the amount of organic matter, but the presence and nature of low organisms that render drinking-water unwholesome. Much difficulty in interpretation of the biological results seems to have arisen from too great differences of absolute strength in the solutions of organic matter used.

SCIENCE AT KHARKOFF¹

THE Society of Naturalists at the Kharkoff University is one of those which were founded a few years ago for the advancement of the natural sciences generally, and especially

¹ *Trudy Obshchestva Estestvoispytatelei pri Kharkovskom Universitete* (Transactions of the Society of Naturalists at the Kharkoff University), vol. xv. 1882.

for the study of the natural history of Russia in the provinces that surround University towns, and which have already rendered most valuable services in both these directions. The Kharkoff Society of Naturalists, which numbers 117 members, has already published fifteen volumes of their Transactions (*Trudy*), which contain many valuable papers. Of those in the earlier volumes we will only mention, in geology: The chemical researches of rocks and coal of the Dnieper basin, by A. S. Brio; geological explorations in the government of Kharkoff and in the Coal-measures of the Don, by A. W. Guroff; and in the basins of the Dnieper and Kalmius, by M. F. Klemm; the explorations of the Delta of the Dnieper, and microscopical analyses of the Dnieper granites and of the fossil trees of Southern Russia, by M. E. Krendovsky; the very interesting researches into the formation and shapes of valleys in Southern Russia; on the crystalline rocks of the Dnieper; on black earth, on the Devonian formation of the Sosna and Tim river, and on the structure of the mountains of Taurida, by Prof. S. F. Levakovsky; and on the hydrography of the Northern Donets river, by J. T. Morozoff. The attention of the Kharkoff zoologists was especially attracted during recent years to the obnoxious insects which destroyed the crops, and we find in the *Transactions* of the Society several papers devoted to the subject, such as a complete description of the locusts and other insects inhabiting corn-fields, by P. W. Ivanoff; on the parasites of the locust and the corn-beetle, by P. T. Stepanoff; and on obnoxious insects of the province of Kharkoff, by W. A. Yaroshevsky. The same author has published also nearly complete lists of the Hemiptera, Heteroptera, Diptera, and Lepidoptera of the province of Kharkoff. Among many other contributions in zoology and physiology we notice physiological researches into the structure of the eyes of birds, on the movements of protoplasm, on the air-sacs of birds, and on the mechanism of their breathing; on the movements of *Unio*, and of *Anguis fragilis* (all with numerous plates), by R. F. Byeletzky; on water-acarides, by M. E. Krendovsky; on the *Bythotrephes* of the Sea of Azov, and on a new *Polyphemida*, by N. P. Pengo; on Infusoriae, Turbellariae, and Lepidoptera of the province of Kharkoff, by Madame S. M. Pereyaslavtseff; on the development of Nematodes, and on *macrobiotus macronyx*, Duj., by the late G. M. Radkevitch; and on the Araneæ fauna of the province of Kharkoff, by W. W. Reinhard. There are but few papers on botany in the *Transactions*. K. S. Gornitsky contributes a "Conspectus plantarum" of the Walki district of the province of Kharkoff; E. M. Delarme has two contributions on the anatomy of Coniferae and on the Kirkazon plants; N. F. Kransakoff publishes a list of plants of the neighbourhood of Taganrog, and Novocherkask; and L. W. Reinhard, on the conjugation of zoospores, and on the Characeæ of Middle and Southern Russia. All these papers are profusely illustrated, and sold each separately at very low prices.

The recent (fifteenth) volume of the *Transactions (Trudy)*, contains the work done by the Society in 1881. M. Stepanoff contributes a paper on the very unsettled question as to the metamorphosis of Bombylides. He has found larvæ of Bombylides in cocoons of *Stauronotus vastator*, Stev.; they support very well temperatures as low as -20° Cels., and can remain at life for more than one year. The opinion of M. Zetterstedt as to the larvæ of Bombylides living also freely, non-parasitically, in the soil, seemed to be confirmed by M. Stepanoff, who found them in the autumn and in the spring in the soil, but they might have already abandoned their former dwellings. M. Stepanoff gives also a complete description (with coloured drawings) of the larvæ of *Systoechus leucophagus*, Mg. —M. Kulchitzky contributes two papers; on the endings and ramifications of the motor nerves of the lower vertebrata (the author doubts that the motor nerves necessarily end in small lamellæ under the sarcolemma, as it was observed by Herr Kühne); and on the origin of the coloured globules of the blood of Mammalia; these last—the author says—arise, not out of protoplasm, but from globules of lymphoid elements which undergo a whole series of very complicated metamorphoses.—M. Yaroshevsky gives a list of Neuroptera and Hymenoptera of the province of Kharkoff. The Neuroptera of the close neighbourhoods of the Kharkoff city number no less than sixty-one species. The Hymenoptera number 400 species, of which no less than 235 are known in the neighbourhood of the Kharkoff city. The same author, in company with M. Sokoloff, contributes a paper on the state of larvæ of the corn-beetle (*Anisoplia*) during the winter. The recent ravages of the corn-beetle in Southern Russia had provoked new researches on this