ON SOME POINTS IN THE ANALYSIS OF WATER, AND THE INTERPRETATION OF THE RESULTS.

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I FEEL some diffidence in reading a paper on such a well-worn subject as water analysis, before a Society of Professional Analysts, but my apology is, that while I may occupy the time of the Society with what some of its members will rightly regard as truisms, the facts brought forward are systematically ignored by many water analysts, and discredit frequently brought upon the profession in consequence.

Any chemist who has had experience in the examination of potable waters, will, occasionally have found a difficulty in pronouncing an opinion on the fitness of a sample for domestic use, when neither pains nor time have been spared in gathering *data* to enable him to come to a definite conclusion. The number of cases in which this difficulty occurs, is greatly increased by the fact, that at the present time, water-analysts may be divided pretty sharply into two groups: those who practice the method of Frankland and Armstrong, and those who employ the process of Wanklyn and Chapman.

The use of one process or another is, in many branches of chemical analysis, a matter of comparative indifference; but in water-analysis, it seems often to be understood to imply a distinct belief in one set of "symptoms," with simultaneous *dis-belief* in another set.

This discreditable and unsatisfactory state of things has its origin in unfortunate differences between the authors of what may fairly be called the rival methods of water-analysis.

Of the two methods, it may fairly be said that Wanklyn's is infinitely the more popular, and is the process in general use. On the other hand it is urged that the popularity of Wanklyn's process is due less to its intrinsic merits, than to its rapidity and facility of execution; Frankland's process being admittedly one of the most delicate operations in the whole range of chemical analysis, and, according to its enemies, incapable of giving accurate results, except by accident.

Of Frankland's method of determining the organic carbon and nitrogen in water, I have not myself had any direct experience, and, owing to the small number of chemists employing it, instances of concordant results having been obtained independently, by the analysis of the sample by different chemists, are difficult to obtain. An instance, however, was made public recently, in which duplicate analyses of the same sample were made independently by Dr. Frankland, and by Mr. J. W. Thomas, Public Analyst for Cardiff. The results of the two analyses agreed closely, and I am acquainted with several other unpublished cases in which equally satisfactory agreements have been obtained.*

It may, however, be fairly open to question, whether Frankland's method would give absolute results in the case of samples containing large amounts of nitrates. It is evidently not sufficient that the sample should give concordant results in the hands of different chemists, but that test experiments should be made on known quantities of some unstable form of organic matter *in presence of a large excess of nitrates*. I am not

* Among the members of this Society, Drs. Campbell Brown and Hill are well-known to employ Frankland's method.

aware that any results bearing on this point have ever been obtained, or at least published, by Dr. Frankland or his disciples, although the objection has been so repeatedly and forcibly urged by Mr. Wanklyn, that it certainly requires some kind of answer.

As to Wanklyn's method of estimating albuminoid ammonia, the possibility of obtaining by it concordant results in the hands of independent analysts, has been repeatedly proved, and although the fact that the results are only comparative, is now fully recognized, the indications are generally regarded as exceedingly valuable.

The difficulty introduced by the fact that different kinds of nitrogenous organic matter yield different amounts of albuminoid ammonia has been greatly exaggerated; for there is every reason to suppose that the number of kinds of nitrogenous organic matter existing in water is extremely limited, and if that be the case, the amount present ought to be tolerably strictly proportioned to the albuminoid ammonia yielded on distillation. Certainly, the opinion of a very large number of chemists who employ Wanklyn's process, is decidedly in favour of it as a means of discriminating between bad and good water, though probably few place in it so implicit a reliance as its authors contend it deserves.

But although Mr. Wanklyn deserves the thanks of chemists for the introduction of his method of determining albuminoid ammonia, he has unfortunately originated a fertile source of discord, and done much to retard the development of water-analysis, by under-rating the value of the oxidised nitrogen as an indication of contamination.

Unfortunately, Mr. Wanklyn's views on water-analysis are accepted as gospel by a large number of medical officers of health, and other "sucking analysts," and his remarks are too frequently interpreted literally, without the judicious qualifications which Mr. Wanklyn himself would be the first to introduce. Thus, a member of our Society holding two appointments as Public Analyst, has expressed his belief that the determination of free and albuminoid ammonia is all that is necessary for forming an opinion on the quality of a drinking water, and he backs that opinion by pronouncing on samples submitted to him *solely* on the results of those two estimations.*

On the other hand, few chemists appear inclined to support the extreme view of Dr. Frankland, that the presence of nitrates in water (in more than minute quality) is absolutely positive evidence of previous contamination of the water by animal matter;—a view which has been contradicted by the researches of Boussingault, who found considerable quantities of nitrates in water in which contamination by animal matter was out of the question.

The grave mistake which is made by those who ignore the value of oxidised nitrogen in water as an indication of previous contamination by animal matter is evident, when it is remembered that 97 per cent. of the combined nitrogen of sewage was found by the Rivers Pollution Commissioners to become converted into nitrates during its slow percolation through a gravelly soil only five feet thick. As, therefore, free ammonia, urea, and the substances which are represented by albuminoid ammonia, are rapidly changed under favourable conditions, with formation of oxidised compounds of nitrogen, it is evident that the omission to regard the latter as indications of previous contamination is practically to ignore any infiltration of sewage, which is not *very* recent. As we

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* It is worthy of notice that the average amount of free ammonia found by Dr. Angus Smith in the rain of country places was upwards of ten times as great as the maximum quality which is found in pure drinking waters, so that average rain-water would inevitably be condemned by the above *soi-disant* chemist, as being contaminated by sewage.

have good reason to believe that the organisms to which we attribute enteric diseases, resist oxidation far more energetically than dead organic matter, it is evident that all trace of free ammonia, and the greater part of the albuminoid ammonia might disappear and yet the water be dangerous to drink.

There is another circumstance connected with the presence of nitrates, especially in the water of shallow wells, which is too often lost sight of.

According to the researches of Pottenköfller and others, much zymotic disease is due to the *alteration of level* of subterranean water. This, of course, is almost synonymous with the level of the water in shallow wells. In dry weather, when the water is low, sewage filtering through the soil from neighbouring ashpits and cesspools becomes thoroughly oxidised, the nitrogenous organic matter and ammonia being converted into nitrates. But in wet weather, the soil being filled with water, the same oxidation cannot take place, and free and albuminoid ammonia appear in the water of the wells. It is evident, therefore, that a change of weather, or other conditions, may so injuriously effect the water as to change what was possibly safe, though of bad antecedents, into what all chemists agree in regarding as positively dangerous.

As pointed out by Dr. Angus Smith, whose views on water-analysis are too little known and appreciated, it is often interesting and important to distinguish between the nitrogen of nitrous acid, and that of nitric acid. As nitrates contain an atom more of oxygen than nitrites, their presence indicates a more complete oxidation and destruction of the organic matter than obtained in the latter case. If all the combined nitrogen of a water exist in the form of nitrates, it is clear that a very thorough oxidation has occurred, and therefore that the contamination is comparatively old or distant. The presence of nitrites, on the other hand, shows that complete oxidation has not occurred, and therefore that the pollution is near at hand or recent. It has also been found that some kinds of organic matter will abstract oxygen from nitrates, reducing them to nitrites, or even to ammonia. Equally, therefore the presence of nitrites indicates a recent contamination. On this account, in studying the history of a drinking water, it is desirable to ascertain whether the oxidised nitrogen exists wholly as nitric acid or nitrites, or whether nitrites are not also present.

Another point on which I believe the practice of late years has been distinctly retrograde, consists in ignoring the loss on ignition. Because the loss of weight which occurs on igniting the residue left on the evaporation of a water cannot be strictly regarded as organic matter, it has become usual to omit the determination altogether. I believe the actual loss of weight is not without its value, especially when taken in connection with the total solid matter. In a good water the loss on ignition is rarely more than one-fifth of the total weight of the residues, but even if the exact loss be disregarded, the ignition often gives valuable information which can scarcely be obtained in any other way short of an estimation of organic carbon and nitrogen by Frankland's method. Thus in presence of much organic matter, the residue blackens, and if it be of animal origin often gives a distinct smell of burnt feathers. Oxidised compounds of nitrogen of course prevent the blackening, but often give rise to an evolution of red fumes. These and similar indications make the ignition test one which the careful analyst cannot afford to omit, especially as phosphates and lead can be looked for in the ignited residue more conveniently and safely than in any other way.

In the discussion which took place—

Mr. Heisch said that there were several things said by Mr. Allen on which he would gladly have made some remarks, but as that would involve a discussion of the whole subject of water analysis, he would confine himself to one point. Mr. Allen said that he (Mr. Heisch) had introduced a delicate test for phosphoric acid, he (Mr. Heisch) repudiated this. Dr. Frankland found that growths were producible by putting together nitrate of ammonia, phosphate of soda and sugar, but he (Mr. Heisch) denied the identity of these growths, with those which he considered due to sewage. Dr. Frankland only saw his growths after they had assumed the condition of mycelium, in which state they could not be distinguished from many other growths. It was at their first formation that they were most characteristic. One of their great peculiarities was, that they did not require the presence of atmospheric air, the first place in which he had observed them being in a liquid, saturated with carbonic acid. The proper way to try the experiment was, to put about 10 grains of the purest sugar in 5 ounces of the water, in a perfectly clean bottle, which it should quite fill, and stopper it down well, then expose it to day light, at a temperature of about 70°; in the course of about 24 hours certain little bodies could be seen floating about which required carefully looking for; the best way was to put a black cloth against the wall, and look at it through the water, these bodies when examined under $\frac{1}{4}$ or $\frac{1}{8}$ th objective, were found to consist of cells, with very brilliant nuclei. If the bottle was shut up a little longer, these cells would be found to group themselves something like a bunch of grapes. The grouping was very peculiar and very different to anything obtained when the bottle was left open. Ultimately the odour of butyric acid became perceptible. The great point was to exclude atmospheric air, as these germs formed without the presence of air, and in the presence of carbonic acid as well; but the bodies which Dr. Frankland found would not form without the presence of atmospheric air, these were always accompanied by bacteria and not by the formation of butyric acid. He, Mr. (Heisch,) had under his notice recently three waters which came from a place where typhoid fever had broken out; chemically he found little difference between them, but in one, when treated as described, these peculiar bodies were found, and he said if either of the waters had anything to do with the fever it must be that one. The people there were up in arms as this water happened to be a pet one, because it was supposed to come from a spring having its origin in a coppice, and was therefore supposed to be as pure as could be, but the fever increased, and Dr. Guy was sent down by the Local Government Board to examine the question, and ultimately he found the origin of the spring to be immediately under a new workhouse, and not far from the cesspools of that establishment. Of the three waters it was only in that one he (Mr. Heisch) found these bodies.

Mr. E. W. T. Jones, had had considerable experience with both the Frankland and Wanklyn processes, but was not wedded to either. Of course they all thanked Mr. Allen for his paper, though he had not brought forward anything which he (Mr. Jones) had not observed or known before, which he thought would be the case with most of those who had had much to do with water examination. No doubt, as Mr. Allen said, the Frankland organic carbon and nitrogen method was one of extreme accuracy and required the greatest care, and was therefore subject to objections from causes not due to the subject itself. He regarded that as the worst feature of the organic nitrogen method. All the circumstances connected with the determination were such as to make one liable

to errors, which would affect the process considerably, whereas by the Wanklyn albumenoid ammonia method you could with due care show that no error took place during the process of analysis. The solubility of carbonate of lime (which he thought was understood by all of them) is something like 3 in 100,000, but he could not see how it bore upon water analysis; it could not affect one at all unless with a view of getting at the constitution of the mineral matter. He held that the data should be taken *collectively* to see whether they agreed with one another. As to the influence of nitrates upon the determination of organic nitrogen, he thought that had been settled by Frankland and others of his school. He himself had obtained good results in the presence of nitrates, which he thought could be decomposed in the way Dr. Frankland said, although there was a danger of leaving some nitrogen in the residue, but, on the whole, he thought the albumenoid process was preferable.

After a few words from Dr. Muter,

Dr. Dupré said that he never omitted any one of the points mentioned by Mr. Allen. He had never had a water in which he could not detect phosphoric acid. One thing he always did, viz., testing the water itself by permanganate—*i.e.*, by taking half a litre of the water, and adding a very small quantity of permanganate; if that is decolorized a fresh quantity is added until the color remains for 1 hour. The proportion of permanganate added at a time contains 0.08 milligram of available oxygen. Sometimes if the history of a water is not known an analyst might be seriously misled, and condemn a water which he would not do if he had known the history of it, but this simple permanganate test would prevent the mistake being made. He had adopted a plan which might be useful to others. One of the great drawbacks of Frankland's process was that you must always have your Sprengel pump in order or have a room you can set aside for it, but if you have to take your pump, &c., &c., to pieces it is a tedious job. He had some success in estimating the carbon and nitrogen by the ordinary combustion process; he simply estimated the amount of carbon by the old oxide of copper method. He took no precaution about the nitrogen. He passed the gas through a carbonic acid tube which he charged with baryta water, and filtered in such a way that no carbonic acid could get at it, dissolved the barium carbonate in hydrochloric acid, and finally converted it into sulphate, 1 milligram of which corresponded to 0.05 milligram of carbon. The nitrogen he estimated in a separate portion by combustion with soda lime, and, if the amount was very small, determined the ammonia produced by nesslerising. He also considered that no water should be passed without being tested by sulphuretted hydrogen. Dr. Dupré concluded by observing that he hoped no one would be prevented bringing the subject forward again because it was old, for all of them might learn something new at each discussion.

Mr. Allen, in replying, suggested that Mr. Heisch's remarks should be published in "THE ANALYST," so that the members might have an opportunity of seeing them in print.