

SOME REMARKS ON THE PERMANGANATE PROCESS IN WATER ANALYSIS.

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THE experiments about to be mentioned were made in my laboratory some years ago, soon after Dr. Tidy read before the Chemical Society a paper in which he proposed certain standards of oxygen absorbed from permanganate solution for the purpose of classifying samples of potable water. In the same paper the author condemned the free and albuminoid ammonia process of Mr. Wanklyn, as being not only uncertain and unreliable, but less delicate in its indications than the permanganate process; and, shortly afterwards, Dr. Frankland, in his book on water analysis, expressed his opinion that the permanganate process was probably the best substitute for the combustion process. The ease and rapidity with which the permanganate process could be carried out led some analysts to adopt it at once, in lieu of the previously almost universal process of Mr. Wanklyn, and analyses of waters were published in the *Chemical News* and elsewhere, without other figures relating directly to their organic constituents than those of oxygen absorbed. The method, as described at the Chemical Society, although an old one, was invested with novelty in as far as its description was accompanied by the proposal of standards for judging the waters tested by it, and this addition rendered its adoption, as a

supposed simple and ready test for organic purity, particularly tempting to medical men and other pseudo-chemists, as well as to many analysts, who had hitherto been in the habit of giving reports on the results of the Wanklyn process, which involves more manipulative skill.

The experiments I now quote were made with a view to showing that the free and albuminoid ammonia process afforded a more delicate and reliable means of judging a water than does the permanganate process, if the methods were to be regarded as alternative, and only one of them to be employed. The appointment, however, of a "Water Committee" of the "Society of Public Analysts," and the issue of the "full instructions" for water analyses that followed, did much to bring about a generally much fuller analysis of waters than the majority of our analysts had been in the habit of making, leaving the permanganate process to remain as one only of many items in the table of results, and I did not publish these experiments.

The results of experience show us more and more the futility of trusting to anything short of a complete examination of waters, and recent communications to our Society demonstrate the fact that even the results of a complete examination often have their meaning wholly changed by local circumstances. In the recent paper of Dr. Dupré and Mr. Hehner, and also in that of Dr. Ashby and Mr. Hehner, it was shown that the free and albuminoid ammonia test in certain cases might, owing to the rapidity with which nitrification takes place, entirely break down. Much more confidence on the other hand, in the results of the permanganate process, was expressed during the discussion which followed one of the papers, which has led me—in continuance of that discussion—to look up the trials I have referred to.

I regret that the permanganate experiments, having been made before the recommendations of our Water Committee, were made at the ordinary temperature of the laboratory, which, in autumn, might be from 50° to 60° Fahr., the precautions otherwise, being those enumerated in Dr. Tidy's description of the method.

URINE AND DISTILLED WATER.

URINE (Parts per 1,000).		OXYGEN CONSUMED (Grains per gallon).				AMMONIA (Grains per gallon).		
		One hour.		Three hours.		Free.	Albuminoid.	
·05	·003	·004	·007	·003
·10	·005	·005	·015	·006
·25	·011	·019	·028	·021
·50	·021	·032	·059	·045
1·00	·041	·052	·121	·105

URINE AND NEW RIVER WATER.

URINE (Parts per 1,000).		OXYGEN ABSORBED (Grains per gallon).				AMMONIA (Grains per gallon).		
		One hour.		Three hours.		Free.	Albuminoid.	
·00	·016	·022	·001	·002
·05	·019	·028	·006	·004
·10	·020	·030	·010	·006
·25	·026	·037	·021	·012
·50	·040	·047	·044	·025
1·00	·059	·071	·091	·054

(CLEAR) SEWAGE AND NEW RIVER WATER.

SEWAGE		OXYGEN ABSORBED				AMMONIA		
(Parts per 1,000).		(Grains per gallon).				(Grains per Gallon).		
		One hour.		Three hours.		Free.	Albuminoid.	
none	·017	·035	·000	·001
2·5	·027	·039	·005	·001
5·0	·029	·041	·010	·003
10·0	·032	·044	·020	·005
20·0	·039	·048	·038	·011
50·0	·047	·053	·092	·025
100·0	—	·074	—	—

The classifications which Dr. Tidy suggested by way of standards were as follows :—

CLASS I. *Waters of Great Organic Purity.*—All waters in which the oxygen absorbed does not exceed ·095 grain per gallon.

CLASS II. *Waters of Medium Purity.*—Waters in which the oxygen absorbed ranges from ·035 to ·100 grain per gallon.

CLASS III. *Waters of Doubtful Purity.*—Waters in which the oxygen absorbed ranges from ·100 grain to ·150 grain per gallon.

CLASS IV. *Impure Waters.*—Waters in which the oxygen absorbed exceeds ·150 grain per gallon.

Looking at the foregoing results it will be seen that distilled water containing five parts of urine in 10,000, or New River water containing one part of urine in 10,000, would thus be classed as water of *Great Organic Purity*. New River water containing one part per 1,000 of urine, or as much as 10 per cent. of raw sewage, would be classed as of *Medium Purity*. On the other hand the free and albuminoid ammonia results cast more than grave suspicion on distilled water, or even on New River water contaminated with one part of urine in 10,000, and on New River water containing from half per cent. to one per cent. of sewage ; while New River water containing one part of urine in 4,000, or two per cent. of sewage, was utterly condemned by the free and albuminoid ammonia process.

The analyses published month by month in the ANALYST of the same water supplies show how great are the periodical variations in oxygen absorbed by water from the same sources, but, at the present moment, as being more strictly comparable for the present purpose, I will refer to the results of the oxygen absorbed by New River water during one year, as shown in the analyses given by Dr. Tidy in the paper already quoted. The proportion of oxygen absorbed by New River water in 1878 varied from ·016 grain per gallon to ·058 grain per gallon. This difference would allow—judged by the oxygen test alone—an addition of one part of urine per 2,000 of water, or an addition of five per cent. of raw sewage, to pass unsuspected, and without infringing the limits of natural variation in the water itself. Presuming the absence of rapid nitrification, a very far less quantity of pollution would, as already indicated, be at once shown up by the increased free and albuminoid ammonia. It was at the time pointed out that the natural variation in oxygen absorbed was in the case of this, and the Thames water, unaccompanied by a similar variation in the ammonia results, and that the albuminoid ammonia varied but slightly, while the oxygen absorbed varied *pari passu* with the organic carbon and nitrogen shown

in Dr. Frankland's analyses. I incline to the opinion that the main cause of this fact is that the greater part of the organic matter in Thames and New River water is of vegetable origin, and affects the free and albuminoid ammonia tests but slightly, these tests being far more delicate as indicators of animal than of vegetable impurity.

It has been very strongly urged that the more ready oxidisability of animal matter enables us to form some discrimination between it and vegetable matter, by making two tests, as in the foregoing experiments, viz.: by allowing the permanganate to act respectively for one hour and three hours. [This method has been, as most of us believe, improved upon still further by altering the times of action respectively to fifteen minutes and four hours, according to the suggestions first published, I believe, in the instructions of the Water Committee of the Society of Public Analysts. But it is not difficult to see—in fact it is obvious—that the deductions drawn from the comparison of such results must often be rendered almost worthless in an absolute sense, by the proportion of vegetable to animal matter present. Where the organic matter is mainly of animal origin, doubtless the high proportion of the oxygen absorbed in the shorter period to that absorbed in the longer period will be boldly shown. But the same quantity of animal matter, together with a larger proportion of vegetable matter, will not reveal itself with like delicacy. In fact, as in the case of the organic carbon and nitrogen, the damnatory ratio of the two in the animal matter may be hopelessly swamped in the innocent ratio of a larger quantity of vegetable matter.

No doubt general standards of all kinds in water analysis are fallacious, and the necessity of circumspection and carefully balanced judgment in framing our reports on waters becomes more and more apparent as additional experience is gathered. I do not for a moment suggest the abandonment of a factor which is of such value as the permanganate process occasionally is as a confirmatory or comparative test, any more than the authors of the recent interesting papers read before the Society would recommend the abandonment of the free and albuminoid ammonia process, because nitrification may sometimes render its results nugatory. But in the absence of very exceptional circumstances, the permanganate process affords us, I venture to believe, far less information on the subject of water pollution than do the other items in our analyses, and in an absolute sense it is in the majority of cases useless. Relatively it may possess value—occasionally considerable value—and is, therefore, not to be neglected; but except for purposes of comparison it appears to be meaningless, and is at the best, as far as I am able to judge, to be looked upon with diffidence.

Dr. Dupré said he was very glad Mr. Dyer had at last consented to give them a paper, and he hoped that other members of the Society would take courage from that and bring their experience forward. The chief value of the Society was lost if the members did not bring their facts before it—every fact might be of value. No member should think that any fact was too insignificant to be brought forward.

Mr. Hehner pointed out that as in one case there were five parts of urine in 100,000. Urine contained about two per cent. of urea, which furnished about half its weight of ammonia, and hence five parts of urine in 100,000 should give .035 gr. of ammonia per gallon. Mr. Dyer, however, only found .007, and he should like to know where the rest had gone to. Another point he wished to refer to was that he was firmly convinced the oxidizable part in sewage was not organised and dead, and it was the non-oxidizable part which was dangerous.

Dr. Dupré in answer to Mr. Hehner said, first—that if perfectly fresh urine were taken no free ammonia and no albuminoid ammonia would be obtained, but after standing awhile much ammonia was obtained by distillation; and, secondly—that they could not judge anything as to the amount of urine added by the ammonia obtained. With reference to Mr. Dyer's paper he (Dr. Dupré) had great faith in the permanganate test; there was no process like it to distinguish a deep from a shallow well water, or to distinguish whether a deep well water was contaminated with surface drainage or sewage. As soon as there was a slight amount of surface contamination into the well evidence of it was obtained by the increased amount of oxygen absorbed. In several cases a water had been sent to him which yielded a very considerable amount of ammonia, but tested by the oxygen it absorbed he felt sure at once it could not be a polluted water. He did not consider urine one of the best substances to experiment on water with. It would seem to him from the results that Mr. Dyer was a very good worker with the ammonia process, but not quite so good with the oxygen process. In the case of ammonia and albuminoid ammonia the results were very fairly proportionate; not so in the oxygen series. One process had worked well and the other not so well.

In the case of the sewage which had been added to the waters it must have been very dilute sewage. He had made a great many experiments, and he found that with anything like five per cent. the oxygen absorbed came to $\cdot 2$ or $\cdot 3$, which was nearly ten times the amount Mr. Dyer had found with twenty parts in 1,000. Therefore, he could not help thinking that the sewage must have been very much diluted.

He did not wish to imply that there was any marked superiority of the one over the other, but what he believed was that taking the two processes together they got exceedingly valuable indications, and carefully applying both they got a good idea of whether the contamination was animal or vegetable, although not by either separately.

They had no means of getting at the absolute amount of organic matter present in a water. Even Frankland's process did not give them that.

Dr. Muter said that for many years he had been a supporter of the permanganate process. Any water that would stand it was a safe water to drink or rather it was better not to drink any water that would run away with the permanganate. As a sort of empirical test it was very good indeed, and one he had always been in favour of. If he were going on a journey he would prefer to take a bottle of permanganate in his pocket to judge a water by rather than anything else.

After all that had been said against it he thought there was no more complete scheme of water analysis before the public than that issued by the Society.
