

XVIII.—*Note on Frankland and Armstrong's Memoir on the Analysis of Potable Waters.*

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IN the memoir lately published\* by Frankland and Armstrong describing the method by which they propose to conduct the examination of waters as regards organic substance, objections are raised to the method we have recommended for determining the relative quality of water by means of the albuminoid ammonia it yields by treatment with alkaline solution of permanganate of potash. Those objections are, to a great extent, based upon a comparison of the results obtained in this way with the results obtained by Frankland and Armstrong's method. We have, therefore, made a careful inquiry into the conditions to which the difference between the results furnished by the two methods may be referred, and into the accuracy of Frankland and Armstrong's method to be applied as a test of the results furnished by our method.

In placing before the Society the conclusions at which we have arrived, we must, in the first place, premise,† as before stated, that we do not consider the complete conversion of organic nitrogen into ammonia by our method as being essential to its applicability for determining the relative quality of water, and that we rely simply upon the constancy of the ratio between the amount of albuminoid substance in the water and the quantity of ammonia produced.

The next point which we have to consider is the degree of accuracy attainable in estimating the carbon and nitrogen in the water-residue according to Frankland and Armstrong's method. In order to enable a judgment to be formed on this point, the authors gave ten examples, in which known weights of known substances were dissolved in distilled water with some carbonate of soda, or carbonate of lime, and the residues obtained, after treatment with  $\text{SO}_2$  and evaporation, were burnt with chromate of lead. In the following tables we give

\* Chem. Soc. Journal (March, 1868.)

† Chem. Soc. Journal (December, 1867.)

the amounts of carbon taken, and the amounts obtained, also the amounts of nitrogen taken and obtained, and the errors applying to each experiment :—

Substance taken.		Carbon taken.	Error.	Carbon obtained.
milligram.		milligram.	milligram.	milligram.
I..	35·2 Sugar	14·82	— 0·19	14·63
II..	34·7 „	14·60	— 0·74	13·86
III..	11·4 „	4·80	— 0·40	4·40
IV..	12·2 „	5·14	+ 0·16	5·30
V..	11·5 „	4·84	— 0·50	4·34
VI..	10· Urea	2·00	— 0·23	1·77
VII..	10·25 „	2·05	+ 0·06	2·11
VIII..	10·4 „	2·08	+ 0·31	2·39
IX..	20·2 „	4·04	+ 0·48	4·52
X..	25· Hippuric acid	15·08	— 1·22	13·86

  

Nitrogen taken.		Error.	Nitrogen obtained.
Milligramme.			Milligramme.
V.....	2·46	+ 0·08	2·54
VI.....	4·66	— 0·03	4·63
VII.....	4·78	— 1·21	3·57
VIII.....	4·84	— 0·16	4·68
IX.....	9·42	— 0·55	8·87
X.....	1·95	+ 0·08	2·03

From these tables it will be seen that there is a deficit of carbon in six out of the ten determinations, and an excess in four of them. The greatest error in deficit is 1·22 milligram.; the least error in deficit is 0·19 milligrams.; the mean error on the six determinations being 0·49 milligrams. In ordinary organic analyses, wherein 200 or 300 milligrams. of a substance such as sugar is taken, it is possible to obtain results which are accurate to within about one-tenth per cent., equal to an absolute error of 0·2 milligram. of carbon. When smaller quantities of substance are analysed in the ordinary way, it is admitted that the degree of *percentage accuracy* attainable is inferior.

The quantities of organic substance to which the results given by Frankland and Armstrong refer are from 10 to 35 milligrams., being about one-tenth as much as would be operated

upon in an ordinary organic analysis. But the absolute error, as shown in the tables above, is from 0.2 to 1.2 milligram. of carbon, so that while operating on smaller quantities there is no corresponding reduction of *absolute* error, and consequently Frankland and Armstrong's method, as exhibited by their own experiments, does not attain to a higher degree of accuracy than would be reached by ordinary organic analysis applied to very small quantities of organic substance.

The importance of this circumstance as regards the estimation of organic substance in a water will be appreciated when it is considered that the quantity of organic substance in a litre of water is seldom anything like so much as the quantities of sugar, &c., operated upon in the experiments given as indicative of the degree of accuracy attainable by Frankland and Armstrong's method.

From the results obtained for nitrogen it will be seen that out of the six experiments the results of four are in deficit, and those of two are in excess. These results apply to quantities of nitrogenous substance fully ten-fold as large as those likely to be present in a litre of ordinary water. It, therefore, appears to us that taking these data as representing the extent to which this method can be depended on for the determination of the minute quantities of carbon and nitrogen in a water-residue, it does not estimate quantities of nitrogen which fall short of half a milligramme. Now, on turning to the table of analyses at the end of the memoir,\* it will be seen that the quantity of organic nitrogen per litre (and a litre is the quantity of water upon which the determinations were made) is represented as ranging from 0.00 through all varieties of intermediate value to 0.56 milligram. These quantities of nitrogen are, however, within the limits of error indicated by the experiments above referred to; consequently, we cannot regard these results as representing differences of quality in the different kinds of water.

Having thus considered what are the capabilities of the method proposed by Frankland and Armstrong we will now proceed to discuss the comparison which they institute between the results furnished by our method and those obtained by their own. In the first place it will be seen that the differences

\* Chem. Soc. Journal, March, 1868, p. 108.

between the results of the two methods observed by Frankland and Armstrong, range from + 0.05 to - 0.52 of a milligramme, amounts which, as we have already shown, lie within the limits of experimental error.

From these differences, therefore, no conclusion of any kind can be drawn, and we consider it to be sufficiently evident that Frankland and Armstrong's method is incapable of testing the accuracy of the results obtained by our method as stated below.

	Milligramme per litre.	
	Albuminoid NH <sub>3</sub> , Wanklyn, Chapman, and Smith.	Organic Nitrogen. Frankland and Armstrong.
Bala Lake water .....	0.25	0.01
Loch Katrine water .....	0.13	0.08
Manchester water .....	0.07	0.26
Thames water as delivered in	0.06	0.48
London by the different com-	0.15	—
panies at different dates .....	0.12	—
	0.14	—
	0.20	—
New River water ....	0.084	0.14
	0.09	—
East London Water Company....	0.09	0.24
Caterham water.....	0.00	0.07

On general grounds we are disposed to consider that the circumstance of Frankland and Armstrong's method being applicable only to the residue obtained by evaporation of a water, is a disadvantage, both as regards the time requisite for making an experiment, and on account of the probability of loss of organic substance. But, in our opinion the preliminary treatment of the water with SO<sub>2</sub> in order to eliminate nitrogen existing as nitrates and nitrites comprises a source of error of a far more serious character. There can be no question as to the complete expulsion of CO<sub>2</sub> by this treatment, and we therefore pass over that part of the subject. But as the nitrogen existing as nitrates in some kinds of water is often much more than ten times as much as the nitrogen existing in organic states of combination, it will be manifest that the estimation of organic nitrogen by Frankland and Armstrong's method,

would become illusory, if only a small portion of the nitrates were to escape decomposition.

On referring to Frankland and Armstrong's paper it will be seen that, the process for the destruction of the nitrates and nitrites is as follows:—"2 litres are poured into a convenient stoppered bottle, and 60 c.c. of a recently prepared saturated solution of sulphurous acid are added." . . . "One half of this sulphurized water is now boiled for two or three minutes, and unless it contained a considerable amount of carbonates, 0.2 gm. of sodic sulphite is to be added during the boiling, so as to secure the saturation of the sulphuric acid formed during the subsequent evaporation." The addition of "a couple of drops" of solution of ferrous or ferric chloride is also recommended, and the water is subsequently to be evaporated to dryness upon a steam or water-bath.

The authors remark further on, that "such an expulsion of the nitrogen of nitrates and nitrites is a remarkable reaction, and could scarcely have been predicted; indeed it takes place to a very partial extent only when a nitrate is dissolved in water, and evaporated with excess of sulphurous acid in imitation of a natural water; neither is the result very different when sodic chloride, or calcic or magnesian carbonate is added."

We agree with the authors in looking upon a total decomposition of a *nitrate* by a few minutes' boiling with a solution of sulphurous acid as remarkable. On the other hand a decomposition of free *nitric acid* by sulphurous acid is what we should be quite prepared to expect.

When it is considered that a litre of many waters contains in solution sufficient free oxygen to generate 0.06 gm. of sulphuric acid by oxidation of the sulphurous acid, it will become obvious that, notwithstanding the addition of the 0.2 gm. of sodic sulphite, which is recommended in the case of those waters containing no considerable amount of carbonates, there will always be great danger of the water becoming strongly acid. The probability of the 30 c.c. of saturated solution of sulphurous acid containing sulphuric acid is also great; there is, moreover, the risk of absorption of oxygen, and consequent formation of sulphuric acid during the standing in the bottle, and during the boiling in the flask.

It is worthy of note, that the addition of the "couple of drops" of solution of ferric chloride, which the authors find

to be so efficacious in rendering the decomposition of the nitrate complete, is equivalent to an addition of so much free acid.

Of the six experiments given by Frankland and Armstrong to illustrate the *complete* decomposition of the nitrates (pp. 96 and 97), the first one, the third and fourth, are instances in which, from the absence of any alkaline or earthy sulphite to take up the sulphuric acid, there must necessarily have been free nitric acid from the very beginning of the reaction. In the second of these experiments, 10 c.c. of a solution of sodic sulphite (strength unknown) were added. In the fifth experiment a natural water was taken, but no mention is made of the amount of carbonate of lime in it. Only the sixth admits of discussion as a possible example of a complete reduction of nitrates without the charging of the water with free sulphuric acid. In this experiment, .01 grm. magnesia, 0.1 grm. calcic carbonate, 0.1 grm. sodic chloride, 0.01 grm. potassic chloride, 1 drop of solution of ferric chloride, 2 drops of solution of hydric sodic phosphate, 0.1 grm. potassic nitrate, and 15 c.c. of sulphurous acid solution were taken, and complete destruction of the nitrate was the result.

By calculation, it will be seen that the 10 milligrammes of magnesia and 100 milligrammes of carbonate of lime are equivalent to 122.5 milligrammes of sulphuric acid. Now the oxygen dissolved in the water cannot have been less than would suffice to form about 60 milligrammes of sulphuric acid, whilst 97 milligrammes of sulphuric acid would be set free by the reduction of the 100 milligrammes of nitrate of potash. Thus we should have about 34.5 milligrammes of free sulphuric acid as the final result of the reaction.

It would, therefore, appear that in Frankland and Armstrong's test-experiments, in which there was complete reduction of the nitrates, the circumstances were such as to give rise to free sulphuric acid as a final product.

We have made experiments in which care was taken to avoid the production of this acid as an ultimate product of the reaction, and have never succeeded, under such circumstances, in effecting a *complete* destruction of the nitrates. In some instances, iron and phosphates were present in the *natural* waters experimented upon; but still the destruction of the nitrates was incomplete.

The following experiments may be cited:—Water from a pump in Great Portland Street: 1 litre taken, 30 c.c. of a saturated solution of sulphurous acid was added, and then boiled for two minutes; evaporated on the steam-bath (one or two c.c. of a saturated solution of sulphurous acid being added four times during the evaporation). Result: 14 milligrammes of  $\text{HNO}_3$  were left in the residue. It is to be observed that this water contains both iron and phosphates. The water from a pump in Bartholomew Lane gave a similar result.

To another well-water a quantity of sulphite of protoxide of iron was added before submitting it to the action of sulphurous acid, and yet the residue contained much unreduced nitrates.

In another instance, 100 milligrammes  $\text{HNO}_3$  (in the state of nitrate of potash), 300 milligrammes  $\text{Ca}_2\text{O} \cdot \text{CO}_2$ , 100 milligrammes  $\text{KCl}$ , and about 400 milligrammes of phosphate of lime were put into half a litre of distilled water, boiled with 30 c.c. saturated solution of sulphurous acid, and evaporated to dryness. Result: 55 milligrammes of  $\text{HNO}_3$  left undecomposed in the residue.

On repeating this experiment and substituting sulphite of protoxide of iron for the phosphate of lime, 69.5 milligrammes of  $\text{HNO}_3$  was left undecomposed.

In another experiment half-litre of New River water was taken, saturated with carbonic acid, and then boiled, cooled in an atmosphere of that gas, and again boiled and cooled in carbonic acid; in this way it was insured that the water should be free from dissolved oxygen. 15 c.c. of a saturated solution of sulphurous acid, free from sulphuric acid, was then added, and the whole mixture boiled for  $2\frac{1}{2}$  minutes and evaporated to dryness. The residue was found to contain much nitric acid. (These determinations of nitric acid were made by a modification of Schulze's aluminium-process, a description of which has been laid before the Chemical Society.)

From all these experiments two facts are very apparent. First, the operation of destroying the nitrates in water by means of sulphurous acid is a very uncertain one. Secondly, the operation, as practised by Frankland and Armstrong, gives rise to free sulphuric acid in the residue. We need hardly add that few organic substances will bear being heated to  $100^\circ \text{C}$ ., with their own weight of sulphuric acid, without undergoing great decomposition.

We must here call attention to the circumstance that in the experiments made to determine the degree of accuracy attainable by Frankland and Armstrong's method of estimating carbon and nitrogen, no nitrates were added to the water, and as there was in all cases sufficient alkaline or calcareous sulphite to take up any sulphuric acid produced by oxidation of sulphurous acid by the oxygen dissolved in the water, there was no charring of the residue by sulphuric acid. In this very material condition, therefore, the trial experiments differ from those made to prove complete destruction of nitrates, and from operations on natural water.

In the case of water containing large quantities of organic nitrogen, as for example actual sewage in which the amount of nitrogen would be capable of estimation by Frankland and Armstrong's method, we encounter another difficulty, due to the presence of ammonia in the water residue.

In order to arrive at the organic nitrogen, it would then be necessary to make a determination of the free ammonia in the water, and to deduct the nitrogen corresponding to it from the total nitrogen of the residue. Owing, however, to the circumstance that ammonia would be lost by diffusion during the evaporation (even in presence of an acid), the water-residue will contain only a part of the original ammonia, and consequently an error would arise in deducting the amount of nitrogen corresponding to the original ammonia, from the total nitrogen of the residue.

This source of error would, of course, affect to some extent all determinations of organic nitrogen in waters containing free ammonia, but it would become important in the case of such waters as London well water, which often contains a considerable quantity of free ammonia.

We will conclude by giving in a tabular form a number of analyses made by our ammonia-method, showing the extreme constancy of the results. Each of the first five sets of analyses bracketed together was made on the same day, on the same sample of water.



Name of Water.	Quantity operated upon. Litres.	Milligrammes of Albuminoid Ammonia per litre of the water.
West Middlesex water .. {	$\frac{1}{2}$	0.070
	1	0.065
	$1\frac{1}{2}$	0.07
Southwark and Vauxhall.. {	1	0.20
	1	0.205
	$\frac{1}{2}$	0.19
	$1\frac{1}{4}$	0.18
Well at Wimbledon .. {	$1\frac{1}{2}$	0.21
	1	0.15
	$\frac{1}{2}$	0.16
Bishopsgate-street pump.. {	1	0.24
Mixed with equal volume of distilled water .. .. {	$\frac{1}{2}$	0.255
	$\frac{1}{2}$ (= 1 litre of mixture).	0.26
Thames water above Hampton .. .. {	$\frac{1}{2}$	0.21
	1	0.21
	$1\frac{1}{2}$	0.205
Manchester water all taken at same date, but from different parts of the town {	$\frac{1}{2}$	0.06
	$\frac{1}{2}$	0.07
	$\frac{1}{2}$	0.07
Edinburgh water taken from a tap at the University on 18th and 19th Sept., 1867 {	1	0.075
	$1\frac{1}{2}$	0.063
	1	0.070

London Institution.