DETERMINATION OF CARBON AND NITROGEN IN POTABLE WATERS IN THE WET WAY.

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The accurate determination of both carbon and nitrogen in potable waters in the wet way is evidently very desirable. Its practical execution, however, is attended with great difficulties. In respect of the carbon, it has been proposed either to measure the carbon dioxide expelled on boiling with an oxidizing agent, or to measure the amount of reduction of the oxidizing agent itself.

For the estimation of the nitrogen it has been proposed to convert it into ammonia, and nesslerize the distillate. In the treatise of A. W. Blythe on Foods, p. 535, I find the following account of a process by Mr. Smethan (*Analyst*, Sept., 1880, p. 156), in which the first method of estimating carbon is employed: "A liter of the water under examination is acidified with phosphoric acid, and concentrated to 50 c.c. It is then oxidized by means of an oxidizing mixture, consisting of 1 grm. of potassium bichromate, 1 grm. of potassium permanganate, and 20 c.c. of sulphuric acid, of 1.4 sp. gr. The liquid is then boiled, and the carbon dioxide condensed in an absorption tube on similar principles to those adopted by Dupie and Hake, the barium carbonate being ultimately determined as sulphate. In Mr. Smethan's paper there are full details, and the test experiments with known weights of sugar, benzoic acid, isinglass, picric acid and urea appear to be very satisfactory."

A similar plan is proposed by Dr. Burghardt (*Chem. News*, 1886, p. 271), the oxidation being effected by boiling with a very large excess of chromic acid or potassium bichromate and sulphuric acid. The evolved carbon dioxide is absorbed in flasks containing standard calcium hydrate, and the excess of alkali titrated with decinormal oxalic acid. Furthermore, the carbon dioxide given off is collected in four separate successive portions, and ascribed to as many separate origins.

1st. That given off by heating for a quarter of an hour at 94° C., which is set down as *dissolved* carbon dioxide.

2d. That given off by heating the water until the steam given off raises the calcium hydrate in the first of the two absorption flasks nearly to boiling. This is set down as carbon dioxide evolved by the *decomposition of the organic matter.*

3d. That given off by raising the residue from the second operation boiling, after addition of 20 c.c. of dilute sulphuric acid, stated as being "mostly that derived from *calcium and magnesium carbonates in the water.*

4th. That derived by boiling the residue from operation third with 5 grms. of chromic acid and 20 c.c. sulphuric acid. "The carbon dioxide evolved in this stage is derived entirely from *organic carbon present in the water.*"

In a subsequent paper (*Chem. News*, 1887, p. 121), Dr. Burghardt substitutes for the measurement of the CO_2, evolved by boiling in presence of a large excess of chromic and sulphuric acid, the measurement of the reduction in a standard dilute chromic acid solution. Instead of using 5 grms. of chromic acid to effect the oxidation, but 0.2 grms. is used in the example given.

It is evident that there are great difficulties in estimating the organic carbon in potable waters by measuring the reduction of the oxidizing agent. The reagent which thus far has given best results is potassium permanganate. But this is decomposed when either in alkaline or acid solution ; slowly on standing and rapidly on boiling. Moreover, at whatever temperature it is employed and whether in acid or alkaline solution, the reduction corresponds neither to the entire carbon, nor to a definite fraction thereof. I believe that all attempts to employ permanganate other than as a convenient indicator of approximately the relative amounts of organic matters present in potable waters have been abandoned.

Perhaps the most carefully studied of these processes was that proposed by Wanklyn and Chapman in 1878. They used :

1. Potassium permanganate—1 c.c. equivalent to 1 mgrm. O.
2. Ferrous sulphate solution—1 c.c. equivalent to 1 c.c. permanganate.
3. 5 p. c. caustic potash solution.
4. Dilute sulphuric acid.

5 c. c. of the potash and 5 c.c. of the permanganate were added to a liter of the water and the mixture then boiled down to about

700 c.c. The reduction of the permanganate was estimated by the ferrous sulphate. Dr. Burghardt proposes to employ the following solutions:

1st. Ordinary decinormal potassium permanganate (3.16 grms. to 1 liter).

2d. Chromic acid (about 10 grms. per liter).

3d. Ferrous sulphate (about 25 grms. per liter).

To this a fourth should be added, standard oxalic acid, because the "oxygen value" of the permanganate cannot be assumed. The chromic acid must be titrated with the sulphate, and the latter by permanganate. The only test of the process which is given is one upon a sample of sewage.

To study the working of the process upon an ordinary potable water, the following trial was made:

1 c.c. $KMnO_4$=0.0008 O.
10 c.c. $KMnO_4$=8.5 c.c. $FeSO_4$.
8.5 c.c. $FeSO_4$=0.008 O.
10 c.c. CrO_3=22.0 c.c. $FeSO_4$.

250 c.c. of a natural water was taken, boiled one half hour with 50 c.c. CrO_3 and 10 c.c. H_2SO_4, and then made up to 1 liter. 100 c.c. of this solution=10.9 c.c. $FeSO_4$.

50 c.c., CrO_3=110 c.c. $FeSO_4$.
110—109=1 c.c. $FeSO_4$.=0.94 mgrm. O.

This is equivalent to 0.141 parts of carbon per 100,000.

But all such tests are eminently unsatisfactory. A solution of quinidine sulphate of known composition was therefore prepared. 8.24 mgrms. of this salt, equivalent to carbon 4.74 mgrms., and nitrogen corresponding to ammonia 0.70, were dissolved in 250 c.c. of ammonia-free water. 25 c.c. of the chromic and 10 c.c. of the sulphuric acid were added and the mixture boiled for half an hour. It yielded 3.18 mgrms. carbon. 400 c.c. of this liquid after making up to the liter were distilled with 5 grms. soda, until 250 c.c. distillate came over. This was nesslerized, yielding only 0.234 mgrms. ammonia.

A second experiment using precisely the same quantities of the salt gave no carbon and 0.312 mgrm. ammonia.

A third gave 3.35 carbon and 0.225 ammonia.

The same amount of quinidine sulphate was then taken, but the quantity of chromic acid was increased to 0.50 grm. A fourth trial yielded no carbon and 0.200 ammonia. Repeated and obtained no carbon; the ammonia lost.

The quinidine sulphate was increased to 16.48 grms., corresponding in the amount of liquid used to 9.88 mgrms. carbon and 1.40 mgrm. ammonia. The sixth experiment, with same amounts of reagent as in Nos. 4 and 5, yielded 0.35 mgrm. carbon and 0.640 ammonia. Repeated and obtained 0.35 mgrm. carbon and 0.740 mgrm. ammonia.

These results were so unsatisfactory that I abandoned the process, and substituted potassium permanganate in acid solution for the oxidizing agent, and instead of estimating the reduction, determined the evolved carbon dioxide. This is virtually employing the process of Kjeldahl, so far as the estimation of the ammonia is concerned.

The apparatus employed consisted of a 2 liter retort, with arrangements for passing air, previously freed from carbon dioxide, ammonia and dust through it; a condenser, and two flasks for absorbing the carbon dioxide in decinormal baryta, provided with suitable guard tubes.

In the first trial of this process, 1 liter of water containing 8.24 grms. of quinidine sulphate was introduced into the retort the atmosphere changed by aspiration and 250 c.c. of water distilled off. This distillate proved to contain a minute amount of carbon dioxide derived from the distilled water employed. Then this having been got rid of, 1 grm. of $KMnO_4$ and 10 c.c. H_2SO_4 were added and an additional 400 c.c. distilled over. The 50 c.c. of baryta solution in the absorption apparatus showed that 13.72 mgrms. CO_2 had been evolved, corresponding to 3.74 mgrms. C. A third distillate of 100 c.c. contained 3.6 mgrms. $CO_2 = 0.98$ mgrms. C, making the total carbon 4.72 mgrms. instead of 4.94 mgrms., the amount used.

On adding caustic soda to the residue in excess and redistilling, 0.624 mgrm. of ammonia were obtained of the 0.70 mgrm. required by theory.

This result was encouraging inasmuch as Wanklyn's method yielded only 0.335 mgrm., or a little less than half.

Another trial was made using 500 c.c. distilled water, 1 grm. $KMnO_4$ and 10 c.c. H_2SO_4. The water and permanganate were first vigorously boiled in a flask to drive off CO_2 and NH_3 ; the H_2SO_4 was added and the boiling continued in order to get rid of any traces of chlorine in the permanganate. Then the quinidine sulphate was introduced, the atmosphere of the retort changed and the distillation carried on until the contents of the retort were reduced to a small bulk. The distillate contained 5.11 mgrms. of carbon, as against the theoretical 4.94. 90 c.c. of a solution containing 23 grms. of soda, after vigorously boiling with 300 c.c. of water to expel traces of ammonia, were added to the residue in the retort, 400 c.c. distilled over, the distillate made up to a liter and nesslerized. It yielded 0.65 mgrm. NH_3 : theoretical 0.70 mgrm.

The process was further tested by subjecting a solution containing 0.1 p.c. of pure sugar to similar treatment. The amount of carbon theoretically present in the half liter used was 4.215 mgrms. In four successive experiments 4.66, 4.95, 4.39 and 5.20 mgrms. were obtained. A new blank experiment was then made and a small amount of CO_2 obtained, showing that the probable source of this constant plus result was a slight air leakage into the apparatus.

A test was then made upon a brown swamp water, containing much peaty matter but no sewage. One liter was acidified with 2 c.c. H_2SO_4 and 250 c.c. distilled off. The distillate contained 15.51 mgrms. CO_2. 100 c.c. of a previously boiled solution containing 1 grm. $KMnO_4$ and 10 c.c. H_2SO_4 were added and 500 c.c. distilled off. It yielded 93.6 mgrms. CO_2=25 mgrms. carbon.

The residue distilled with excess of soda evolved 0.90 mgrm. ammonia. These results give for the carbon-nitrogen ratio 27.7 to 1, in case the first portion of carbon dioxide which came off is regarded as dissolved and combined CO_2.

On repeating the experiment, 11.04 mgrms. dissolved and combined CO_2 (?) were obtained, and 26.66 mgrms. evolved after addition of acid and permanganate. The ammonia was 1.15 mgrm., corresponding to a $\frac{}{N}$ ratio 26 to 1.

A similar trial with the city water (from the Hackensack river) gave for the dissolved and combined CO_2 (?) 36.74 mgrms., for the organic carbon (?) 4.77 mgrms. and the organic nitrogen 0.28 mgrm., or a ratio of 17 to 1.

The process was further tested upon a solution of amygdalin. Ten mgrms. of this substance dissolved in 1 liter of water, yielded 4.759 mgrms. of carbon and 0.206 mgrm. nitrogen, instead of 4.696 mgams. carbon and 0.274 mgrm. nitrogen as required by theory. A second trial, using the same amount of amygdalin, gave 4.845 mgrms. carbon and 0.181 mgrm. nitrogen. The failure to obtain with substances of known composition the theoretical yield of ammonia ; the difficulties connected with all attempts to distinguish between the carbon dioxide derived from organic carbon and that from dissolved and combined carbonic acid ; the nature and magnitude of errors in the nitrogen determination arising from the influence of the chlorides, nitrates, etc., in potable waters, all these factors conspire to render the process of attempting to determine the carbon and nitrogen in the wet way so unsatisfactory and uncertain that I desisted from the attempt. I desire to acknowledge, in the performance of these experiments, the co-operation of my assistant, Mr. W. G. Johnston.