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ON THE DETERMINATION OF THE ORGANIC NITROGEN IN NATURAL WATERS BY THE KJELDAHL METHOD.

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THE justification for the almost universal practice of determining the organic nitrogen in waters in the form of albuminoid ammonia is to be found in the great simplicity of the Wanklyn process. The amount of nitrogen obtained in the form of ammonia by the action of alkaline permanganate on nitrogenous organic matter in water bears no known relation to the total nitrogen present, and chemists report widely differing results in consequence of differing practice. In the case of colorless waters, with small amount of organic matter, the differences are not usually great, but in most surface waters, with considerable organic matter in suspension and solution, the results often differ fifty or one hundred per cent. Some water analysts stop the distillation for albuminoid ammonia when 150 c.c. have distilled over; others continue until 250 c.c. are obtained, and again, others strive to get all the ammonia they can by the addition of more alkaline permanganate, or by replacing the water which has distilled over.

There can be no doubt that the determination of the total organic nitrogen would be generally practised in place of the determination of the albuminoid ammonia, if there was available a short, easily executed, and accurate method for this purpose.

As the result of a very large number of experiments with the Kjeldahl nitrogen process, we think it may be safely said, that this method leaves little, if anything, to be desired in these respects.

The modifications of the process, as usually practised, to adapt it to the determination of organic nitrogen in waters, are in the direction of its simplification. Thus, the amount of organic matter in water is ordinarily so very small that the use of solid potassium permanganate for the final and complete oxidation of the organic matter is probably never necessary. In most of the analyses which we have made, we have continued to use it as a matter of precaution, but in the comparative experiments, with and without its use, the results have not differed. The volumetric determination of the ammonia by titration with very dilute standard acid was found to be less accurate and less convenient than the Nesslerization of the distillate, in the usual method employed in water analysis. Further, the same flask is used for both the digestion and the distillation.

Professor W. R. Nichols experimented with the Kjeldahl process for the determination of the nitrogen in sewage with satisfactory results,* but the process has not yet, far as we know, been used in regular water analysis.

The examination is conducted as follows: 500 c.c. of the water is poured into a round-bottom flask, of about 900 c.c. capacity, and boiled until 200 c.c. have been distilled off. The "free ammonia" which is thus expelled may, if desired, be determined by connecting the flask with a condenser. To the remaining water in the flask is added, after cooling, 10 c.c. of pure concentrated sulphuric acid.† After shaking, the flask is placed in an inclined position on wire gauze, on a ring-stand, or other convenient support, and boiled cautiously, in a good-drawing hood, until all the water is driven off and the concentrated sulphuric acid is white or a very pale yellow. The flask is then removed from the flame, and a very little powdered potassium permanganate added until, on shaking, the liquid acquires a green color, showing that an excess of the permanganate has been added. Should the color be purple instead of green, it shows that the water has not all been driven off. After cooling, 200 c.c. of water free from ammonia are added, the neck of the flask being washed free from acid, and then 100 c.c. of sodium hydrate ‡ solution. The flask is immediately connected with the condenser, and then shaken to mix the contents.

The distillation at the start is conducted rather slowly, and the first 50 c.c. are condensed in very dilute hydrochloric acid.§ The contents of the flask may then be boiled more rapidly until 150 c.c. to 175 c.c. have altogether been collected. The total distillate is made up to 250 c.c. with water free from ammonia, well mixed, and 50 c.c. taken for Nesslerization. No serious difficulty has been encountered from bumping when boiling the alkaline solution. The use of metallic zinc in the

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* Franklin Institute Journal, August, 1885.

† It is necessary to have for this purpose sulphuric acid which is very nearly, if not quite, free from nitrogen in any form. Baker & Adamson, of Easton, Penn., make an acid for this purpose which contains only ~~.05~~ milligram of ammonia in 10 c.c. .005

‡ The sodium hydrate solution is made by dissolving 200 grams of commercial caustic soda of good quality in 1.25 litres of distilled water, adding two grams of potassium permanganate and boiling down to somewhat less than a litre. When cold, the solution is made up to a litre. The addition of the permanganate is to oxidize any organic matter which may be present in the caustic soda.

§ This acid should be free from ammonia: 1 c.c. of the acid is equivalent to 0.5 milligram of ammonia.

flask to facilitate the boiling is, of course, inadmissible, on account of the reduction of nitrates and nitrites, should they be present, to ammonia.

Any efficient condensing arrangement may be used for the collection of the ammonia. We have used with great satisfaction the condenser devised by Prof. S. W. Johnson, of the Connecticut Agricultural Experiment Station, which is described in Bulletin No. 12, of the United States Department of Agriculture, Division of Chemistry. It consists of a copper tank, 20 inches high, 32 inches long, 3 inches across the bottom, widening to 6 inches at the top. The tank is provided with an adequate supply of running water, entering at the bottom, and accommodates 6 or 7 block-tin condensing-tubes three-eighth inch internal diameter, which enter the tank through holes in the front side near the top, above the level of the overflow, and pass down vertically through the tank and out through rubber stoppers tightly fitted into holes in the bottom. They project about 2 inches below the tank, and are connected by means of rubber tubes to straight glass calcium-chloride tubes with a bulb at the upper end. These glass tubes dip into 250 c.c. flasks which receive the distillate. The distilling-flasks are connected with the tin condensing-tubes, by means of rubber stoppers which carry a bulbed-glass tube bent at right angles. This tube and its rubber stopper remain permanently connected with the tin tube.

The flasks rest on iron rings, and are heated with the free flame of a Bunsen burner. They should be carefully selected as to size and height, and the fixtures should be so arranged that all parts are interchangeable. There is then never any difficulty in putting the flasks promptly into place and connecting them with the condenser.

It is a good plan to have flasks, partly filled with water free from ammonia, connected with the condensing-tubes when not in use.

Before beginning a determination, the water in the flask is boiled until the distillate shows, on Nesslerization, that the apparatus is completely free from ammonia. Into the flask which receives the distillate there is put 1 c.c. of the dilute hydrochloric acid and 50 c.c. of water. The delivery tube dips into this liquid only during the collection of the first 50 c.c. of the distillate. The flask is then lowered so that the tube remains above the liquid for the remaining time of the distillation.

In carrying out the operation, the most scrupulous care must be observed in preventing access of ammonia from any source. The acid solutions will absorb ammonia from the air of the laboratory or from the dust of the room if they are allowed to remain uncovered for any length of time. This source of error has been found at times to be very large;

quite enough to render a determination valueless. One experiment gave a gain of ammonia in twenty hours, by leaving the flask which contained the concentrated sulphuric acid uncovered, equivalent 0.5 c.c. of the standard ammonium chloride solution, and at another time the gain was 3 c.c.

The operation should, therefore, be carried out without interruption, and for every determination, or set of determinations, a blank analysis with ammonia-free water should be made for a correction for the ammonia in the reagents and that accidentally introduced in the process.

We have not found that the presence of nitrates and nitrites in waters interferes with the accurate determination of the organic nitrogen. The error which has been found by Kjeldahl and Warrington * to be caused by nitrates in the determination of organic nitrogen seems to disappear under the conditions of great dilution which we have in natural waters.

The following experiments bear on this point: —

1500 c.c. standard ammonium chloride solution (= 15 milligrams NH_3) and 10 c.c. of standard potassium nitrite solution (= 1 milligram N) were boiled with 10 c.c. of sulphuric acid, and the vapors condensed. This distillate contained only 0.15 milligram nitrogen as ammonia and nitrous acid. The residue in the flask was made alkaline and distilled, and the ammonia obtained was precisely the amount taken; namely, 1500 c.c. The experiment was repeated, using a nitrate in place of the nitrite, and under the same conditions the 1500 c.c. of ammonia were recovered.

When a smaller amount of ammonia was used, we still failed to observe any loss. Thus when 10 c.c. standard ammonium chloride solution and 10 c.c. potassium nitrite solution (= 0.1 milligram N) were treated as above, there was obtained ammonia equivalent to 10.5 c.c. Another experiment with the same quantities gave precisely 10 c.c. of ammonia regained. With potassium nitrate instead of nitrite, in the same proportions as in the foregoing experiment, 10.5 c.c. of ammonia were obtained.

The attempt to collect all the nitrous and nitric acids in the distillate was unsuccessful. The flask and condenser were connected by ground joints, so that the distillation could be continued after the sulphuric was concentrated. Owing, probably, to the shape of the flask, the acids were condensed, in part, in the neck of the flask, for after a second and a third addition of water and a renewal of the distillation more nitrous and nitric acids were obtained in the distillate. To see whether there

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* Chemical News, 52, p. 162.

was any loss of ammonia from ammonium sulphate in presence of sulphurous acid from the action of sulphuric acid on carbonaceous matter, the following experiments were tried: 10 c.c. of standard ammonium chloride solution were treated with 10 c.c. of sulphuric acid and a weighed amount of Swedish filter paper. Deducting for the nitrogen in the paper, determined in a blank analysis, 10.5 c.c. of ammonia were obtained. In a duplicate experiment the ammonia obtained was 10 c.c.,— precisely the amount taken. In still another experiment with 50 c.c. of standard ammonium chloride solution and filter paper, 51 c.c. were obtained.

No attempt has been made to compare, as regard the results obtained, the above-described method of determining the organic nitrogen with the combustion method of Frankland and Armstrong. But the following experiments on very dilute solutions of organic substances of known composition may serve to confirm the accuracy of the method.

One hundred milligrams of pure crystals of urea were dissolved in one litre of water free from ammonia. Ten cubic centimetres of this solution were added to 500 c.c. of water and the analysis conducted as above described. There was obtained 0.494 milligram, the theoretical amount being 0.466. In a duplicate experiment no solid potassium permanganate was added to complete the oxidation, and the result was 0.486 milligram.

A solution of uric acid in dilute potassium hydrate was made of the same strength as the urea, and 10 c.c. taken for analysis. There was found 0.326 milligram of nitrogen; required, 0.333 milligram. In a duplicate experiment without the permanganate — precisely the same amount was obtained.

A solution of naphthylamine, 100 milligrams to the litre, was dissolved by the aid of dilute hydrochloric acid. An analysis of 10 c.c. gave 0.082 milligram nitrogen; required, 0.097. Here, again, the result obtained by the omission of the permanganate agreed precisely with the determination in which the permanganate was used.

The following series of experiments made on a sample of Cochituate water shows the very close agreement of results in the determination of organic nitrogen under varying conditions. From a large bottle of water freshly drawn from the tap, were taken five portions of 500 c.c. each.

The first portion was treated by the usual method, already described.

The second portion was treated like the first, except that the addition of solid permanganate was omitted.

The third portion received 10 c.c. of standard potassium nitrate solution, equivalent to 0.1 milligram of nitrogen.

The fourth portion received 1 c.c. of potassium nitrite solution, equivalent to 0.01 milligram of nitrogen.

The fifth portion contained ten times the amount of potassium nitrite as the fourth portion, or 0.1 milligram.

The third, fourth, and fifth portions were treated in all respects like the first portion.

The results, expressed in organic nitrogen, parts per 100,000, were : —

No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
0.0354	0.0354	0.0354	0.0365	0.0365

It may be of interest to give a few of the results obtained in the determination of the organic nitrogen by this method in natural waters in comparison with the results obtained as albuminoid ammonia. In the table following will be found the analyses of some Massachusetts waters during three successive months, June, July, and August, 1888.

In the first column is a record of the color, based on a comparison with the Nesslerization of a known amount of ammonium chloride. Thus a color 1, means that the water possessed a color corresponding in depth and tint to 1 c.c. of standard ammonium chloride solution (=.00001 gr. NH_3) when Nesslerized; a color of 2 is twice the depth of color, and 0.1 is one-tenth the color of 1. In the second column is the albuminoid ammonia obtained by the adding 40 c.c. of alkaline permanganate to the water in the flask, after boiling off 150 c.c. for free ammonia, and then distilling over 250 c.c. In the third column is the organic nitrogen determined by the Kjeldahl process, converted into ammonia to make the figures comparable with the second column. All the determinations were made on the waters filtered through paper in the laboratory.

COMPARISON OF ALBUMINOID AMMONIA AND ORGANIC NITROGEN IN NATURAL WATERS.

I. SURFACE WATERS.

Water.	Color.	Albuminoid Ammonia.	Organic Nitrogen calculated as Ammonia.
Arlington, Reservoir —			
June	.8	.0256	.0560
July	.3	.0274	.0560
Boston Supply, Basin 4 —			
June	1.0	.0226	.0470
July	.7	.0234	.0400
August	.9	.0254	.0460
Boston Supply, Basin 2 —			
June	1.4	.0350	.0590
July	1.3	.0294	.0450
August	.85	.0234	.0440
Boston Supply, Basin 3 —			
June	1.9	.0392	.0790
July	1.7	.0336	.0540
August	.8	.0278	.0590
Boston Supply, Lake Cochituate —			
June	.35	.0176	.0420
July	.10	.0192	.0390
August	.10	.0196	.0420
Boston Supply, Mystic Lake —			
June	.20	.0252	.0590
July	.10	.0244	.0560
August	.15	.0212	.0420
Bridgewater, Taunton River —			
June	2.3	.0248	.0520
July	1.0	.0210	.0440
August	.7	.0212	.0390
Brockton, Reservoir —			
June	.9	.0234	.0570
July	.9	.0260	.0490
August	.7	.0310	.0610
Brookline, Charles River —			
June	1.20	.0320	.0520
July	.60	.0216	.0470
August	.45	.0208	.0380
Cambridge, Fresh Pond —			
June	.20	.0162	.0370
July	.15	.0170	.0390
August	.0	.0172	.0390

Water.	Color.	Albuminoid Ammonia.	Organic Nitrogen calculated as Ammonia.
Clinton, Nashua River —			
June	.1	.0072	.0230
July	.2	.0144	.0360
August	.2	.0124	.0320
Fitchburg, Reservoir —			
June	.1	.0124	.0250
July	.1	.0158	.0340
August	.1	.0146	.0240
Great Barrington, Housatonic River —			
June	.1	.0122	.0320
July	.1	.0120	.0270
August	.0	.0134	.0320
Nashua, Merrimac River —			
June	.4	.0120	.0320
July	.2	.0132	.0290
August	.2	.0106	.0290
Lowell, Merrimac River —			
June	.30	.0142	.0420
July	.10	.0148	.0280
August	.25	.0134	.0320
Haverhill, Merrimac River —			
June	.40	.0164	.0490
July	.20	.0170	.0420
August	.20	.0163	.0348
Lake Winnepesaukee —			
June	.0	.0090	.0230
July	.0	.0082	.0190
August	.0	.0080	.0200
Hyde Park, Neponset River —			
June	.6	.0286	.0520
July	.8	.0432	.1100
Lynn, Birch Pond —			
June	.45	.0194	.0420
July	.35	.0216	.0410
August	.25	.0174	.0410
Malden, Spot Pond —			
June	.3	.0216	.0440
July	.2	.0198	.0390
August	.2	.0216	.0390

Water.	Color.	Albuminoid Ammonia.	Organic Nitrogen calculated as Ammonia.
Montague, Connecticut River —			
June . .	.15	.0120	.0220
July . .	.20	.0118	.0250
Springfield, Connecticut River —			
June . .	.4	.0132	.0390
July . .	.15	.0146	.0320
August .	.15	.0170	.0380
New Bedford, Acushnet River —			
June . .	2.3	.0296	.0540
July . .	1.8	.0278	.0540
Northboro, Assabet River —			
June . .	.7	.0192	.0490
July . .	.4	.0216	.0380
August .	.4	.0174	.0410
Salem, Wenham Lake —			
June . .	.10	.0132	.0320
July . .	.05	.0118	.0290
August .	.00	.0130	.0260
Springfield, Ludlow Reservoir —			
June . .	.10	.0222	.0460
	.20	.0214	.0440
July . .	.10	.0220	.0420

Water.	Color.	Albuminoid Ammonia.	Organic Nitrogen calculated as Ammonia.
August	.05	.0198	.0390
	.10	.0206	.0370
Wayland, Reservoir —			
June . .	1.5	.0272	.0590
July . .	.9	.0364	.0660
August .	.4	.0244	.0540
Whitman, Hobart's Pond —			
June . .	1.7	.0538	.0990
July . .	1.5	.0426	.0990
August .	.9	.0342	.0740
Wilmington, Shawsheen River —			
June . .	.8	.0242	.0640
July . .	.15	.0114	.0370
August .	1.00	.0316	.0570
Woburn, Horn Pond —			
June . .	.35	.0290	.0570
July . .	.25	.0324	.0590
August .	.10	.0240	.0440
Worcester, Blackstone River —			
June . .	—	.0350	.1350
July . .	—	.0440	.1550
August .	—	.0830	.3800

II. GROUND WATERS.

(*Without Color.*)

Water.	Albuminoid Ammonia.	Organic Nitrogen as Ammonia.
Brookline, Filter Gallery —		
June	.0046	.0190
July	.0046	.0220
August	.0042	.0170
Newton, Filter Gallery —		
June	.0044	.0190
July	.0072	.0160
August	.0052	.0100
Revere, Wells —		
June	.0018	.0034
July	.0034	.0070
August	.0018	.0100

Water.	Albuminoid Ammonia.	Organic Nitrogen as Ammonia.
Revere, Reservoir —		
June	.0034	.0130
July	.0046	.0150
August	.0060	.0190
Waltham, Filter Gallery —		
June	.0030	.0170
July	.0050	.0160
August	.0056	.0150
Waltham, Reservoir —		
June	.0042	.0230
July	.0042	.0180
August	.0060	.0160

It will be noted that the organic nitrogen in the surface waters is in general about double the albuminoid ammonia. The average of all the analyses of the waters given above is 0.0214 for the albuminoid ammonia, and 0.0476 for the organic nitrogen. In the ground waters the relation of the albuminoid ammonia to the organic nitrogen is still less. Too much importance must not, however, be given to this relation in the case of the ground waters, for it is probable that the figures given for the organic nitrogen are all a little high, owing to the fact that all of the sources of error were not fully known when most of the analyses were made. The proportional excess in case of the surface waters is believed to be insignificant, but with the smaller content of nitrogen in the ground waters the error is perhaps proportionately large.

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