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THE DETERMINATION OF DISSOLVED ORGANIC NITROGEN IN SEA WATER*

By

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The dissolved organic nitrogen occurring in the sea has so far received the least attention of all the nitrogen-containing fractions. As Krogh (1) has pointed out, it is present in relatively large amounts but is apparently unavailable for use by living organisms. The present investigation was carried out to test the practicability of a more extensive study of the distribution and significance of the dissolved organic N in the sea.

The method employed has been described by Krogh and Keys (2). A sample of 5 ml. of sea water is introduced into a silver combustion tube, which contains a pellet of pure KOH and through which a stream of purified oxygen-free hydrogen is passed. The extended tip of the tube dips into 1 ml. of dilute HBr solution. The water is first distilled off by gentle heating, after which the tube is heated along its entire length to about 500° C., which transforms the organic nitrogen into ammonia. Then 2 ml. of "nitrogen-free" water are introduced and the process repeated, since the salt residue tends to retain some ammonia. The ammonia driven over into the HBr solution is then determined according to Krogh's modification of Teorell's method (3). In a separate sample of sea water pre-formed ammonia must be determined according to Krogh, and this value subtracted from that obtained in the total nitrogen determination. A blank correction must also be applied, since it is impossible to procure water entirely free of dissolved organic N. It occasionally happens that, for some reason, the ammonia is incompletely driven off. To guard against this source of error a blank run on 2 ml. of the "nitrogen-free" water is made after the analysis of each sample.

We found that it is possible with this procedure to carry out a series of four analyses and blanks without opening the combustion tube.

The method requires practice before satisfactory results are achieved. In Table I we give the analytical data from two sets of determinations, in order to illustrate the accuracy that can be

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TABLE I

COMPARISON OF SUCCESSIVE DETERMINATIONS ON TWO DIFFERENT SAMPLES OF SEA WATER. ONE MICROGRAM OF N CORRESPONDS TO 0.56 ML. OF NAPHTHYL RED

Sample	Titration: ml. of naphthyl red			Dissolved organic $N + NH_3$ in γ per l.
	Blank	5 ml. sea water	Diff.	
1	2.96	2.27	0.69	246
1	2.95	2.39	0.56	200
1	2.95	2.26	0.69	246
1	2.97	2.35	0.62	222
			Mean	229
2	3.80	3.28	0.52	186
2	3.84	3.28	0.56	200
2	3.79	3.27	0.52	186
2	3.81	3.30	0.51	182
			Mean	189

expected. The first is a set of average accuracy that can be obtained without great difficulty; the accuracy of the second series is obtained only after long practice, and is even then not always achieved.

A further test of the accuracy of the method was made by analyzing 6 samples of sea water 16 times each, in sets of 4 analyses at a time. All these samples had been stored in the laboratory, at room temperature and in the light, for over one year. Aged sea water was chosen, since it could be assumed that no further changes in the content of dissolved organic N would occur during the time of the analysis (1 day to 1 week). It could therefore be expected that differences in the results were due to analytical errors only. We have then calculated the mean value of the 16 determinations of each sample and the percentage deviation of each set of 4 analyses from this mean. Table II shows that the error of a set of analyses will in

TABLE II

AVERAGE DEVIATIONS IN PER CENT, IN SIX DIFFERENT SAMPLES OF SEA WATER. EACH SERIES CONTAINS FOUR ANALYSES. AVERAGE DEVIATIONS FROM THE MEAN OF SIXTEEN DETERMINATIONS

Station Depth	3354 0m	3515 0m	3245 0m	3245 800m	3245 1200m	Misc. >1000m
Series 1	+3	-5	-5	-11	+5	-8
Series 2	-3	+12	± 0	+6	-4	+4
Series 3	-3	-9	+2	-4	± 0	-2
Series 4	+3	+3	+3	+8	-1	+6

general be well below 10%. The accuracy of the method should be enough to decide whether or not the distribution of dissolved organic N is as uniform as Krogh assumes. Table III shows the absolute values found in these and in two other samples of aged sea water. These are of some interest, since they can be compared with Krogh's fresh samples. The average of our four surface samples is 147 γ per liter; that of the 4 deep samples 214 γ . This latter figure is close to Krogh's value of 244 γ for a whole deep water column, possibly within experimental error. The values for surface water are, however, decidedly lower. Whether this is due to a stratification of the dissolved organic N in the sea, or to disappearance of nitro-

TABLE III
DISSOLVED ORGANIC N IN AGED SEA WATER SAMPLES
MICROGRAMS PER LITER

<i>Station</i>	<i>Depth</i> <i>m</i>	<i>Age of</i> <i>sample</i>	<i>Organic</i> <i>N+NH₃</i>	<i>NH₃</i>	<i>Dissolved</i> <i>organic N</i>
3354	0	16 mo.	158	0	158
3515	0	15 mo.	111	6	105
1474	0	7½ yrs.	173	45	128
3245	0	18 mo.	266	70	196
3245	800	18 mo.	238	16	222
3245	1200	18 mo.	249	10	239
1474	3000	7½ yrs.	216	8	208
Misc.	>1000	22 mo.	185	0	185

genous substances during storage, must be decided by later observations.

The method can hardly be used on ship board. It was therefore necessary to ascertain the conditions under which samples can be satisfactorily preserved for analysis after return to the laboratory. Tests were carried out on two samples of harbor water, which were analyzed immediately after sampling and again after storage for various periods under conditions indicated in Table IV. In the case of filtered samples stored in the ice box, or kept either in the dark or the light at room temperature, it seems likely that the differences between the single sets of analyses are due to analytical errors rather than to actual changes. The same applies probably to the unfiltered sample kept in the light. If the content in particulate matter is high, however, and if such a sample is stored in the dark, a considerable, but slowly diminishing, amount of dissolved organic N accumulates. This is due to the fact that under these conditions the organisms die quickly and a large part of their body substance

TABLE IV

DISSOLVED ORGANIC N IN SAMPLES OF SEA WATER STORED UNDER DIFFERENT CONDITIONS. NOT FILTERED. IN LIGHT AT ROOM TEMPERATURE

Conditions	Storage time, days	Micrograms per liter		
		Organic N+NH ₃	NH ₃	Dissolved organic N
Filtered*	0	147	23	124
Dark	7	177	16	161
In refrigerator	12	158	20	138
	22	146	17	129
	28	170	16	154
Not filtered	0	147	23	124
Light	14	168	8	160
Room temperature	23	151	10	141
	28	175	4	171
Filtered*	0	189	80	109
Dark	6	170	37	133
Room temperature				
Filtered*	0	189	80	109
Light	6	129	9	120
Room temperature				
Filtered*	0	189	80	109
Dark	7	152	22	130
In refrigerator				
Diatoms added	0	189	80	109
(318 γ /liter)	4	507	138	369
Dark	9	486	209	277
Room temperature	14	545	265	280

* With No. 4 sintered-glass filter.

goes into solution. Later, it is transformed into ammonia by bacterial activity.

For future investigations therefore, we recommend that samples of about 250 ml. be immediately filtered through No. 4 sintered glass and stored at once on ice in glass-stoppered bottles. Analysis should be carried out as soon as possible. Under these conditions differences of the order of 50 γ per liter are significant.

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