

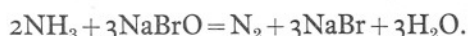
NOTE ON A METHOD FOR DETERMINATION OF AMMONIA IN SEA WATER

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Since the estimation of ammonia in sea water by existing methods either presents difficulties or requires much time, an alternative based on a different principle has been explored.

This method depends upon the action of ammonia on sodium hypobromite in an alkaline medium, when



If the sea water is acidified before the hypobromite is added, the ammonia present will not react. The effect therefore may be measured of adding the hypobromite, in equal quantities, to two samples of sea water, one untreated and one acidified. The difference represents an equivalent of ammonia. Excess hypobromite is estimated colorimetrically by adding Bordeaux B dye solution, which is decolorized by the hypobromite in acid solution.

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THE METHOD

Solutions Required

(i) Hydrobromic acid 0.23N, containing 1.9% HBr. (ii) Sodium hypobromite 0.001N, made by diluting 0.1N stock solution, which is prepared by dissolving 2.5 g. NaOH and 1.25 ml. fluid bromine in 500 ml. of distilled water. This 0.001N-NaBrO is made alkaline by adding 1% of 2N-Na₂CO₃. (iii) Bordeaux B, 0.014 g. of dye per litre. (iv) Ammonium sulphate: stock solution; 0.4716 g. (NH₄)₂SO₄ per litre; working solution is obtained by diluting 4 ml. of stock solution to 500 ml. 0.25 ml. of this solution contains 2 μg. ammonia-N.

Procedure

Exactly 50 ml. of the sea-water sample is transferred to each of three 100–150 ml. flasks by pipette. Using an all-glass syringe (Krogh's pipette) there is then added to

flask A: 1 ml. of (i) solution, followed immediately by
2 ml. of (ii) solution, followed immediately by
5 ml. of (iii);

flask B: 2 ml. of (ii) and then after 1 min.
1 ml. of (i) followed immediately by
5 ml. of (iii);

flask C: 0.25 ml. of (iv) (which is equivalent to the
addition of 40 mg. ammonia-N/m.³) and
thereafter as for flask B.

The flasks are allowed to stand covered for 2 hr. or more (overnight) and the absorption of blue green light is then measured. Colorimetric measurements are conveniently made in a 4 cm. cuvette in the instrument described by Harvey (1948), the light passing through two Ilford filters, no. 404R + no. 403R.

If α , β and γ is the increase in optical density over that of distilled water, of the contents of the three flasks in the same cuvette, then $\beta - \alpha = K \times$ hypobromite destroyed by ammonia present in the water sample, and $\gamma - \beta = K \times$ hypobromite destroyed by the added 40 mg. ammonium-N/m.³.

The concentration of ammonia in the sample of sea water is therefore $\frac{40(\beta - \alpha)}{\gamma - \beta}$ mg. ammonia-N/m.³.

Example

The following shows a typical analysis carried out in triplicate on a sample of sea water collected from offshore:

Difference in Optical Density in 4 cm. Cuvette, Compared with Distilled Water

Exp.	α	β	γ	$\frac{40(\beta - \alpha)}{\gamma - \beta}$ of mg. ammonia-N/m. ³
I	0.305	0.338	0.381	30.7
II	0.302	0.335	0.376	32.2
III	0.298	0.332	0.380	28.3
IV	0.306	0.339	0.374	37.7

The values of α in this experiment indicated that 64 % of the added dye had been decolorized.

The α value varies with the concentration of hypobromite solution, which

decreases with age; it also varies with different sea-water samples, being greater for harbour waters.

The value of $\gamma - \beta$ bears a strict linear relation to the quantity of ammonia nitrogen added up to a total of about 140 mg. N-NH₃/m.³ present. The estimated value of ammonia nitrogen is not affected by the addition of 10 mg./l. of glucose and is not significantly affected by the addition of 40 mg. nitrite nitrogen per m.³. When amino-acetic acid is added, about 30% of the amino-nitrogen behaves as ammonia. During storage the ammonia content of unfiltered sea waters was found to decrease, as had been observed by Redfield & Keys (1938).

Comparison with Determinations Made by Distilling Sea Water in a Current of Air under Reduced Pressure

The method of Krogh (1934) was followed, 30 ml. of sea water (at pH 10-11 obtained by adding 0.25 N-NaOH, using cresol phthalein as indicator) being distilled in a current of air at a pressure of 70-80 mm. mercury.

The use of a 0.006% solution of potassium indigo disulphonate, instead of naphthyl red, gave a sharper end-point and obviated the necessity of titrating each sample at the same speed and of thoroughly cleaning the titration vessels in order to rid them of all traces of oxidation products of naphthyl red. Traces of these products interfere with the titration (Buljan, 1951).

It was found that if amino-acetic acid was added to the sea water, 16-20% of the amino-nitrogen distilled over as ammonia. Hence in both methods, the estimated values for ammonia nitrogen include a part of any amino-nitrogen present. Determinations carried out by the distillation method, in duplicate from the same sample of unfiltered sea water, did not show close agreement, sometimes differing by as much as 11 mg. ammonia-N/m.³.

The following table gives results (in mg. ammonia-N/m.³) obtained by the two methods:

	By distillation	By photometric method
Raw unfiltered sea water collected offshore	29.9	37.7
	35.6	30.7
	25.3	32.2
	21.8	28.3
	Mean 28.15	32.2
Another unfiltered sea water collected offshore	18.1*	25.5
Stored water	16.8*	7.5
Water from Plymouth Sound	27.8*	30.8
Polluted sea water (a mixture of water from densely populated aquarium and open sea water)	40.6*	48.0
Plymouth Sound sea water with artificially destroyed ammonia	3.9	0.0
Total of means	135.35	144.0

* Mean of duplicate determinations.

The totals of the mean values, obtained by each method, are similar. Differences between replicate values appear to be due to similar experimental errors inherent in both methods.

The photometric method is more simple and rapid than distillation.

The time available for this investigation did not allow further study of discrepancies between the two methods.

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