This paper not to be cited without prior reference to the author

International Council for the Exploration of the Sea

C.M. 1969 / C: 8
Hydrography Committee
Ref. L (Plankton C.)

Determination of Total Nitrogen in Natural Waters by means of Persulfate Oxidation

by Folke Koroleff
Institute of Marine Research,
Helsinki

The amount of total nitrogen in unpolluted waters will rarely exceed 5 - 30 µg.at.N / liter. The determination of such amounts by a procedure applicable to routine analysis presents great difficulties, and the ultraviolet light oxidation method is recommended if at all possible. For those laboratories where this equippemt is not available a direct chemical approach my still be necessary. Strickland and Parsons, in their "A Practical Handbook of Seawater Analysis" (1968), have combined a micro Kjeldahl treatment with a determination of the resulting ammonia according to Richards and Kletsch (1964), however, a Kjeldahl digestion is not a routine procedure, especially for ship-board use.

At the Council Meeting last year the author presented a paper on the determination of total phosphorus in natural waters by means of persulfate oxidation (C.M. 1968 / C:33, Hydrography C.). That method has been used successfully at several institutes and on board research vessels. As organically bond phosphorus can be oxidized one can assume that nitrogen of organic substances can be oxidized with persulfate also. That this is the case will be shown in this paper.

General Reactions: The nitrogen compounds in a water sample are oxidized to nitrate by boiling with an alkaline persulfate solution. Excess of oxidant is destroyed according to the

reactions:

$3\ S_2O_8^{2-} + I^- + 6\ OH^- \longrightarrow 6\ SO_4^{2-} + IO_3^- + 3\ H_2O$

$IO_3^- + 5\ I^- + 6\ H^+ \longrightarrow 3\ I_2 + 3\ H_2O$

$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2\ I^-$.

The solution is neutralized and nitrate formed determined as nitrite after reduction in a Cd - Cu column (15 cm) according to Wood, Armstrong and Richards (1967).

Oxidation Agent: 3.0 grams of potassium peroxydisulfate (persulfate) is dissolved in 450 ml of 0.075 N NaOH solution. The persulfate should't contain more than 0.001 % N. A suitable reagent is Merck no. 5092. Stored cold in a dark glass stoppered bottle the mixture is stable for at least a week. This and other solutions mentioned in the procedure, should be made in ammonia-free distilled water.

Procedure: To 10.0 ml of sample in a 100 ml conical flask of Jena or Pyrex glass is added 15 ml of the oxidizing agent. The mixture is boiled in a small heating mantle (Electrothermal) for about 20 minutes, or until the volume is reduced to ca. 10 ml. To destroy remaining persulfate 2.5 ml of 1 percent NaI solution is added and the heating continued for a few minutes more. Allow the mixture to cool for ca. 5 minutes before adding 2 ml of 0.3 N HCl solution. Iodine is now liberated and precipitation dissolves. Let cool to room temperature. Add dropwise 0.1 % sodium sulfite solution to destroy the iodine. Now add ca. 20 ml of distilled water and one drop of 0.05 % phenolphtalein indicator. Titrate to a pale pink color with 0.1 N NaOH solution. Swirl vigorously during the titration and avoid an excess of the hydroxide. By adding a knife-edge of $NaHCO_3$ (ca. 100 mg) the pH is adjusted to 8. Dilute to 50 ml with distilled water and reduce to nitrite in a Cd-Cu reductor. 20 ml is used to wash out the column and nitrite determined in a 25 ml portion.

To prolong the life on the reductor Prof. Sugawara and co-workers (Progress Report of the Preparation of CSK Standard Chemical Solutions, Part III, May 1968) have suggested the following procedure: About 200 ml of EDTA washing solution is passed through the column before use. Then 400 ml of samples, sea water as such or other samples adjusted to pH 8, are passed through. Then the

reductor is treated again with the wshing solution by which the column is reactivated. This procedure has been used successfully on board the Finnish R/V Aranda, both for the direct determination of nitrate and for samples treated according to the method given here.

The determination of blank is essential and must be performed daily. With air as reference the absorbance in a 2 cm cell is 0.18 to 0.25. For 25 ug.at.N / liter the absorbance, corrected for blank, has been ca. 0.450 (2 cm), so the sensitivity of the procedure is satisfactory.

As the procedure contains several steps were contamination from ammonia is like to disturbe, the accuracy of the method can't be better than about ± 10 per cent.

Discussion: At the beginning of the investigation it was tried to oxidize the organic nitrogen compounds according to the procedure for total phosphorus. The results, however, were erratic, especially with sea water samples. Most probably part of the nitrate ions formed were vaporized with the free chlorine developed. In an alkaline solution oxidized Cl-compounds remain in the solution. Surprisingly ammonia is evaporated to 20 per cent only, the remaining 80 per cent being oxidized to nitrate. The rate of oxidation is constant to ± 1 percent. This has to be noted in the calculations.

The method has been tested with various amounts of EDTA, thiourea, thiocarbamate, glycine and pyridine added to distilled and to sea water. The recovery as nitrate was 98 - 100 per cent. It my be mentioned that EDTA can't be oxidized to more than 80 % with U.V. radiation.

As our laboratory has no U.V. equippment and as Kjeldahl digestions are not performed as routine, six membrane filtered samples of various origin were sent to NIVA (Norwegian Water Research Institute) for comparation. The author wish to express his gratitude to Mr. Arne Henriksen for his valuable help.

The results are given in the table. Amount of nitrogen is expressed in micrograms of N per liter.

Sample		a		b		b - c	c	
		(NO_3+NO_2)-N		Tot. - N		Org.N+NH_3-N	Kjel.-N	NH_3-N
o/oo	S	NIVA	IMR	NIVA-UV	IMR	NIVA	NIVA	IMR
River w.	-	0	2	185	142	185	165	10
Rain. w.	-	125	120	410	400	285	250	88
Baltic	7.7	130	136	290	290	160	160	78
Baltic	8.6	65	70	285	265	220	170	66
North Sea	20.6	35	35	325	335	290	255	175
Barents	34.2	140	140	640	630	500	465	420

There is a rather good agreement between total nitrogen values determined according to the procedure given, and those obtained with ultra violet radiation. Surprisingly the Kjeldahl digestion technique seems to give lower values.