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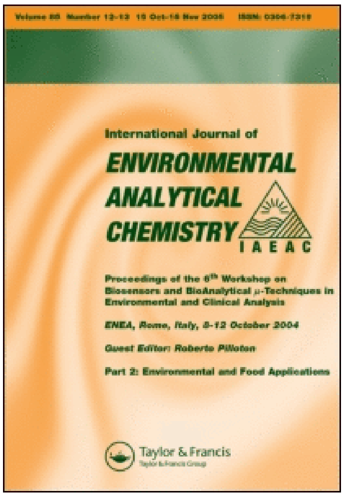

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Determination of Organic Nitrogen in Natural Waters by Means of an Ammonia Probe

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The use of an ammonia probe for the determination of total nitrogen in river and sea water is described. The ammonia is directly determined in the diluted destruction mixture, so that the time-consuming distillation procedure is avoided. Destruction procedures, which mainly differ in the nature of the used catalyst, were compared. The procedure of Gibs and Moum yielded the best results and was adapted for the low nitrogen content waters.

The difficulties encountered when adapting the method and the probe characteristics are reported. The accuracy of the method was checked by comparing it with a well-established titration method and with a colorimetric method. The final procedure allows good precision and accuracy. The limit for precise measurements is around 0.5 ppm N, so that for sea water the method is not universally applicable.

KEY WORDS: Water, sea water, potentiometry, ammonia, total nitrogen, organic nitrogen.

INTRODUCTION

Recently, ammonia probes have become commercially available. These electrodes contain a hydrophobic gas-permeable membrane, which separates the internal solution from the sample solution. A glass electrode measures the pH variation of the internal solution film at its surface due to the diffusion of ammonia through the membrane. The resulting potential is related to the ammonia concentration in the sample. One of the most interesting applications of such probes is the direct determination of NH_4^+ in a Kjeldahl destruction mixture. Bremner and Tabatabai[1] reported the use of the ammonia probe for the determination of organic nitrogen in soils. The determination of organic nitrogen in flour is discussed in a newsletter of one of the electrode manufacturers (Orion Newsletter, 1972). The present paper describes the use of such probes for the determination of total nitrogen in river and in sea water.

EXPERIMENTAL

Apparatus

Ammonia probes EIL 8002-2 and Orion 95-10.
Orion digital 801 pH-meter.
The measurements were performed at 25°C ± 1 in a thermostated polythene recipient.

Reagents

All the reagents were prepared with ammonia-free water.
Catalysator mixture: 950 g of anhydrous Na_2SO_4, 15 g of $CuSO_4 . 5H_2O$ and 20 g of black Se, as described by Gils and Moumm.[2] To stock solutions of glycocol, $CHCl_3$ was added as a preservative.

Procedure

Transfer 5 or 10 ml of sample containing from 1–15 mcg/ml to a 100-ml Kjeldahl flask. In the 0.5–1 mcg/ml range one always uses 10 ml. Add 1 g of the catalyst mixture and 1 ml of concentrated sulphuric acid. Swirl the flask to obtain a suspension. Heat for 30 min. Allow the flask to cool. Add 20 ml distilled water while the flask is warm to prevent the formation of a deposit. Transfer to a 100-ml calibrated flask and adjust to the mark with ammonia-free water. Transfer a 50-ml aliquot of the solution to the polythene recipient. Add 6 ml of 3M NaOH solution. Mix rapidly. The pH of the solution should then be 11.5. Insert the ammonia probe into the solution, stir the solution moderately for 6 to 8 min and record the potential. Calculate the N content using a calibration curve prepared by dissolving $(NH_4)_2SO_4$ in a blank destruction mixture. For the analysis of sea water a blank destruction of synthetic sea water is used.

Note: Smoking should not be allowed in the laboratory since it causes erratic potential readings.

RESULTS AND DISCUSSION

Choice of destruction and measurement procedures

The literature on Kjeldahl determination is very abundant and a large variety of procedures is described. These differ mainly in the nature of the catalyst used. Several catalysts were tried out on solutions of a few ppm N as glycocol. They were:

—procedure I: the catalyst mixture described by Bremner and Tabatabai[1] for the analysis of soils, i.e. K_2SO_4:$CuSO_4.5H_2O$:Se (10:1:0.1). 3 ml of concentrated H_2SO_4 is used together with 1 g catalyst mixture for 5–10 ml of sample.

—procedure II: the procedure described by Martin[3] for sea water consisting of repeated H_2SO_4-H_2O_2 destructions without catalyst.

—procedure III: the method described by Baker[4] using 20 mg of HgO, 2.5 g K_2SO_4 and 1.5 ml of H_2SO_4 for 5 ml of sample.

—procedure IV: the modified method of Baker[4] using iodide to complex the mercury ions.

—procedure V: the Gils and Moumm method[2] using 5 g of catalyst mixture (see experimental) and 5 ml of H_2SO_4 for 5–10 ml of sample.

The results are compared in Table I. It is clear that the best results are obtained with procedure V, which was therefore adopted for further work.

Acceptable results were also obtained with procedure II for concentrations below 2 ppm. Since this is the range in which one usually has to measure when determining the organic nitrogen of sea water or unpolluted river water, this method could be used. However, because repeated digestions are necessary, it was rejected as being too time-consuming. The reasons for the observed errors in the other procedures were not systematically investigated. The possible sources of error are: incomplete destruction, loss of ammonia or non-availability of ammonia for measurement, caused e.g. by complexation with mercury or copper ions.

In some of our preliminary experiments unstable potential readings were obtained. It was found that this was due to the heat of mixing of sulphuric acid and sodium hydroxide. Dilution before the addition of NaOH as described in the experimental section eliminated this source of error. However, because of the dilution needed to reduce the acidity of the sample when using the quantitites as described in procedure V, the sensitivity of the method is limited to 5 ppm. Therefore, to adapt the method to the lower organic N concentrations that often occur in natural waters, smaller quantities of catalyst and sulphuric acid were used (see final procedure in the experimental

TABLE I

Comparison of different destruction procedures

Procedures (see text)	Theoretical N content (ppm)	Found (ppm)
I	6.0	4.6
	12.0	8.0
	24.0	15.5
II	1.0	0.94
	2.0	1.8
	6.0	4.5
	12.0	8.4
	20.0	13.9
III	6.0	4.6
	12.0	7.4
	24.0	15.5
IV	6.0	4.4
	12.0	7.2
	24.0	14.6
V	6.0	5.8
	12.0	11.5
	24.0	23.5

section). It was found that yields of around 95% were obtained in the 0.5 to 15 ppm NH_4-N (see Table II).

TABLE II

Recovery of N using the final procedure

Theoretical (ppm)	Found (ppm)
1.0	1.0
2.0	2.0
3.0	2.8[5]
4.0	3.8
6.0	5.8
12.0	11.6

To obtain standards of the same ionic strength and acidity as the samples, appropriate amounts of blank destruction solutions are used to prepare the standard ammonium solutions. In these circumstances the calibration curves have a nearly Nernstian slope (53–57 mV/decade) in the 0.2–25 ppm NH_4^+ concentration range. At lower concentrations of NH_4^+, the slope becomes gradually smaller. However, at 0.02 ppm NH_4^+ measurements are still possible. If one does not take care of adding approximately correct blank destruction quantities to the standards erroneous results are obtained. If no blank destruction mixture is added at all, errors of approx. 25% are found.

The term "total nitrogen" usually includes organic nitrogen and ammonium, but not nitrate and nitrite. It was verified experimentally that neither nitrate nor nitrite interfere.

Response time and probe lifetime

Under the conditions described here, the probe reaches 99% of the equilibrium potential after 6 min. In solutions containing more H_2SO_4 and NaOH the response time becomes longer. Furthermore, too concentrated acid and alkali solutions damage the membrane and cause unstable measurements.

Using the method described above the probe can be used daily for two months. The slope has then decreased to about 53 mV. Although precise measurements are still possible with such a slope, we prefer to change the membrane when this slope is obtained.

Reproducibility and precision

The reproducibility and precision of the method were determined by multireplicate analyses of synthetic samples. As can be observed in Table II variations of less than 3% are obtained.

Accuracy

To check the accuracy of the method, the results were compared with a well-established titration method for samples of high N content (growing solutions for plant physiological experiments) and with the Nessler or Prochazkova[5] colorimetric methods for low N contents. As can be seen from Table IV one can conclude that the method is accurate. Analogous results were obtained for sea water by comparison of the method which is proposed here with Prochazkova's method.

TABLE III

Multireplicate analysis of synthetic samples

Theoretical N (ppm)	Found (ppm)
1.85	1.8^0– 1.7^5– 1.7^5
2.75	2.7^5– 2.7^5– 2.7^5
3.75	3.7^0– 3.8^0– 3.8^5
4.5	4.5 – 4.6 – 4.6
6.0	6.2 – 6.0 – 5.9
18.0	17.5 –18.0 –18.0
52	51 –51 –51

TABLE IV

Comparison of results by potentiometry with results obtained by classical methods

Growing solutions	Potentiometry (ppm)	Titrimetry (ppm)
1	32.2	32.2
2	31.5	28.5
3	19.8	20.0
4	159	160
5	151	153
6	159	160
7	110	112

Pond water	Potentiometry (ppm)	Colorimetry (ppm)
1	5.3	5.1
2	3.8	4.0
3	3.3	3.3
4	1.3	1.2^5
5	1.4	1.2^5
6	5.8	5.5
7	5.4	6.0
8	5.5	5.6

CONCLUSION

One can conclude that the results obtained by potentiometry show the same precision and accuracy as classical methods. The elimination of the distillation step allows a much more rapid analysis with less attention from the analyst. The method is probably applicable to all types of water, with the exception of ocean water, for which it is not sufficiently sensitive. However, it was used with success for the analysis of coastal sea water and of water from a marine pond.

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References

1. J. M. Bremner and M. A. Tabatabai, *Comm. Soil. Sci. Plant. Anal.* 3(2), 159 (1962).
2. A. Gils and N. Moumm—Serie Technique I.N.E.A.C., No. 54, 16 (1958).
3. D. F. Martin, *Marine Chemistry*, Volume 1: Analytical Methods (Marcel Dekker, N.Y., 1968).
4. P. R. W. Baker, *Talanta* **8**, 57 (1961).
5. L. Prochazkova, *Anal. Chem.* **34**, 965 (1964).