The Use of Ion Specific Electrodes for Chemical Monitoring of Marine Systems

Part I by Richard F. Srna. Charles Epifanio. Michael Hartman. Gary Pruder and Ann Stubbs

THE USE OF ION SPECIFIC ELECTRODES
FOR CHEMICAL MONITORING OF MARINE SYSTEMS

PART ONE

THE AMMONIA ELECTRODE AS A SENSITIVE WATER QUALITY
INDICATOR PROBE FOR RECIRCULATING MARICULTURE SYSTEMS

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INTRODUCTION

At the University of Delaware, as part of a Sea Grant sponsored project to grow shellfish in a recirculating system, a variety of analytical techniques are being evaluated in order to determine their usefulness in mariculture. The criteria for judging the utility of a technique for water quality monitoring include the following:

a) The relevance of the measurement to chemical and biological processes occurring in the growth medium and the rapidity of anticipated concentration fluctuations.

b) The inherent precision and accuracy of the method.

c) The reliability of the procedure and its degree of difficulty.

d) The cost of the analysis in terms of instrumentation required and time necessary to perform the analysis.

Thus the purpose of this work is to evaluate the ammonia ion specific electrode within the framework of its value as a water quality probe in recirculating mariculture systems. The pragmatic questions which were answered involved whether or not the electrode performed adequately in sea water systems, if an electrode could produce data which was consistent with that obtained in other culturing systems using standard ammonia analysis techniques, and how frequently should a recirculating system such as the one at Delaware be monitored.

Within this context, the Orion 95-10 ammonia ion specific electrode was tested, evaluated and incorporated into the analytical facilities.

Theory

A cell EMF, E_{cell}, as generated by an electrode consists of several major contributions given by

$$E_{cell} = E_o + E_m + E_j \qquad (1)$$

Where E_o is a standard potential, E_m is the potential generated across the ion specific membrane, and E_j is the liquid junction potential which results whenever two solutions of different composition come into contact (Durst, 1969). The value for E_m is given by the Nernst equation

$$E_m = 2.3 \frac{RT}{nF} \log \frac{As}{Ai} \qquad (2)$$

where A_i is the activity of the ion in the internal electrode reference solution, A_s is the sample ion activity and $2.3 \frac{RT}{NF}$ is the Nernstron slope which is a constant for a given temperature. Many ion specific electrodes exhibit Nernstran or near Nernstian slopes.

The activity of an ion A_i is related to the concentration of that ion in a solution by the following definition:

$$A_i = \gamma_{\pm} c_i \qquad (3)$$

when $\gamma_{\pm}$ is the activity coefficient and c_i is the analytical concentration of the ion in solution. It can be seen that to the extent that the liquid junction potential, E_j, and activity coefficient are similar in the standard and sample solution, ΔE values may be used to determine the concentration of a substance in solution.

Description

Electrode description: The ammonia electrode is constructed so that a hydrophobic membrane separates the sample solution and an internal filling solution. The membrane allows the passage of small amounts of ammonia gas (and some volatile amines) into the cell body until the partial pressure of the gas is the same on both sides of the membrane. The ammonia, once inside the electrode, reacts with the internal filling solution to produce hydroxide ions. The change in hydroxide ion concentration is detected by an internal reference cell which develops a potential in accordance with the Nernst equation.

Instrumental: In order to obtain sufficient accuracy in measurements using ion specific electrodes, it is necessary to use a high impedance voltmeter, sensitive to at least ± 0.1mv. Several commercially produced instruments are capable of this precision. The cost for such an instrument is under $1,000.00. Table 1 gives the accuracy of concentration determinations resulting from different levels of detection sensitivity of E, the observed electrical potential for divalent and monovalent ions (Durst, 1969).

Table 1

Precision in E	Percent Uncertainty Monovalent	Percent Uncertainty Divalent
0.1 mv	0.4	0.8
0.5 mv	2	4
1.0 mv	4	8
2.0 mv	7.5	15

It can be seen that ion specific electrodes which measure monovalent ions are twice as sensitive as those measuring divalent ions. Since the ammonia gas electrodes actually measure hydroxide ion concentration, its sensitivity is the same as that for monovalent ions.

TECHNICAL CONSIDERATIONS

Electrode drift: Drifting potentials may be caused by a number of factors. These include poor temperature equilibration, inadequate stirring, membrane failure, and an unstable solution concentration. Temperature equilibration is extremely important and involves not only a stable sample temperature but also stable temperature gradients in the portions of the electrode body not immersed in the sample solution. Sample temperature was maintained to an accuracy of $\pm.05°C$. If temperature control was maintained and a millivolt versus time curve did not show an exponential approach to a constant ±0.1 mv value, in a 0.1 m ammonium chloride solution, membrane failure was usually the cause of the difficulty.

Since ammonia is a gas, it can diffuse into the sample from the atmosphere or out of the sample into the atmosphere, depending on relative partial pressures. In order to minimize this problem, samples were measured in 125 ml beakers sealed with rubber stoppers, containing a hole into which the electrode was inserted. Smooth, nonturbulent stirring of the sample with a magnetic stirrer caused acceptably slow variations in sample concentration.

Standard Addition: The standard addition method of analysis was selected for this study, because it is more rapid than preparing standard solution curves and reduces problems of ammonia loss to the atmosphere. The technique provides simple convenient method for determining the exact concentration of a solution whose concentration is known to within an order of magnitude. The theory of standard addition has been detailed elsewhere (Newsletter/Specific ion electrode technology, Vol. II, No. 2, 1970).

In general the following requirements must be met in order to utilize the standard addition procedure:

1) The ionic strength of the solution must remain approximately the same after an addition, e.g., the activity coefficient should not change significantly.

2) There must be no change in the amount of ion pairing or other solution equilibria after the addition.

Tables are available from Orion Research Incorporated which simplify the standard addition calculation and permit rapid calculation of unknown solution concentrations.

EXPERIMENTAL PROCEDURE

The experimental procedure used in this study is based on the one given in the instruction manual for the electrodes. It can be summarized as follows:

Rinse a 50 ml pipette with the sample to be measured. Pipette 50 ml of sample into a 100 ml beaker and equilibrate to $25.00\pm .05°C$. Add

1 ml of 10.m NaOH solution. Place the electrode into the solution and stir slowly using a magnetic stirrer. After 1 minute or when the potential has stabilized to ± 0.1 mv, record the millivolt reading. Pipette 5.0 ml of a standard ammonium chloride solution having approximately ten times the anticipated ammonia concentration. Record the second potential after the electrode has stabilized at the new sample concentration. Using the value of the concentration of the known addition solution and the difference between the potential before and after standard addition, calculate the unknown solution concentration.

The technique requires approximately five minutes per sample analysis.

RESULTS

Precision and Accuracy: Graph 1 shows a plot of experimental potential versus concentration of ammonia at 25.0°C for solutions made from ammonium chloride and distilled deionized water. The measured slope over four orders of magnitude is 58.5, very close to the theoretical Nerstian of 59.16 at this temperature. This data is consistent with that provided by the manufacturer.

Table 2 shows the recoveries obtained using the experimental standard addition procedure described in the previous section for fresh water samples of NH_4Cl solution. Table 3 shows the recoveries obtained in an artificial sea water with added NH_4Cl solution.

A comparison of the data contained in Table 2 and Table 3 indicates that there is no significant difference in the recoveries obtainable in distilled water and sea water at a concentration of 32 ppt.
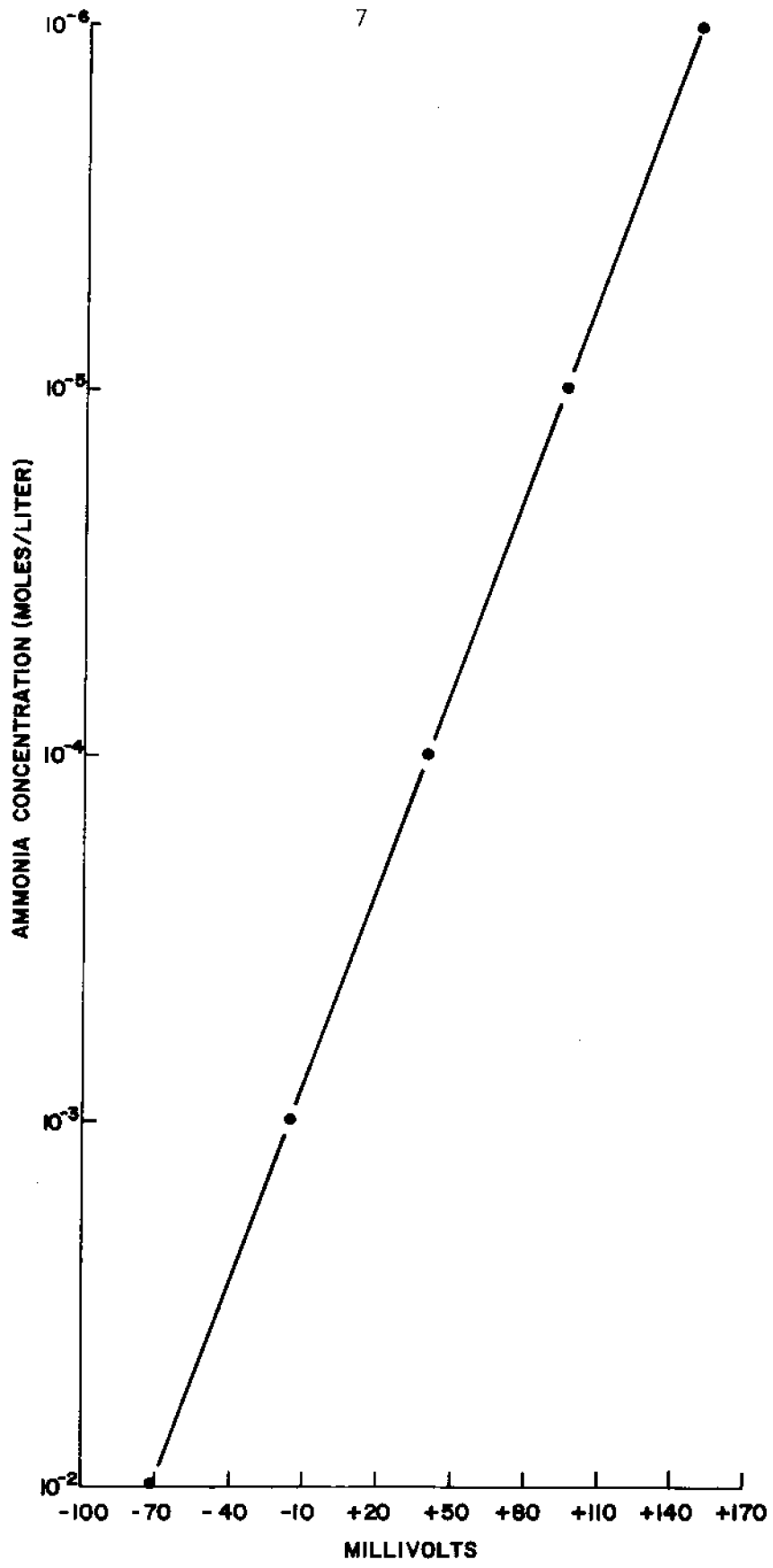
GRAPH I. Ammonia Electrode Calibration

TABLE 2

RESULTS OF STANDARD ADDITION ANALYSIS

OF AMMONIUM CHLORIDE SOLUTIONS IN DISTILLED DEIONIZED WATER

TEST SOLUTION CONCENTRATION (Moles/liter)	STANDARD SOLU-TION CONCENTRATION (Moles/liter)	MILLIVOLTS		CALCULATED TEST SOLUTION CONCENTRATIONS
		Before	After	
1×10^{-6}	1×10^{-5}	140.2	129.7	1.53×10^{-6}
1×10^{-6}	1×10^{-5}	148.2	137.2	1.47×10^{-6}
1×10^{-5}	1×10^{-4}	99.9	83.5	0.92×10^{-5}
1×10^{-5}	1×10^{-4}	97.5	83.0	1.07×10^{-5}
1×10^{-4}	1×10^{-3}	39.9	24.6	1.00×10^{-4}
1×10^{-4}	1×10^{-3}	40.3	25.4	1.12×10^{-4}
1×10^{-3}	1×10^{-2}	-16.7	-31.8	1.02×10^{-3}
1×10^{-3}	1×10^{-2}	-16.9	-32.1	1.01×10^{-3}
1×10^{-2}	1×10^{-1}	-75.5	-90.6	1.02×10^{-2}
1×10^{-2}	1×10^{-1}	-75.5	-90.5	1.03×10^{-2}

TABLE   3

STANDARD ADDITION RECOVERIES

IN ARTIFICIAL SEA WATER

Ammonia Test Solution
Concentrations in
Moles/Liter   Found

1.00×10^{-6}	1.15×10^{-6}
1.00×10^{-6}	$.93 \times 10^{-6}$
1.00×10^{-5}m	1.06×10^{-5}
1.00×10^{-5}m	1.04×10^{-5}
1.00×10^{-4}	1.03×10^{-4}
1.00×10^{-4}	1.01×10^{-4}
1.00×10^{-3}	1.04×10^{-3}
1.00×10^{-3}	1.02×10^{-3}
1.00×10^{-2}	1.02×10^{-2}
1.00×10^{-2}	1.01×10^{-2}

Table 4 shows the results of a statistical analysis of data obtained in seawater.

Applicability: In order to assess the applicability of the ammonia electrode as a water quality probe in mariculture, monitoring of two recirculating systems and one flow-through system containing Delaware Bay water was undertaken.

The graphs demonstrate that data on the changes in ammonia concentration during the conditioning of a biological filter can be obtained using an ammonia electrode. The nitrite concentration data is also shown. The nitrite concentrations often show peaks a short time after an ammonia peak. This is presented as good evidence that the recorded ammonia peaks are real since the behavior of nitrifying bacteria populations is well known. Delaware Bay water was also monitored at the same time as the measurements of the recirculating systems. This was done in order to provide a convenient comparison since ammonia and nitrite concentrations in the Bay were not expected to fluctuate rapidly or over as wide a range as in a recirculating mariculture system.

Graph 2 shows the plot of the ammonia and nitrite concentration in a recirculating system as a function of time. Nitrite concentration was determined according to the method in Strickland and Parsons (1968). The tank being monitored held 8000 liters of sea water and contained a subgravel type biological filter. Sixteen kilograms of locally caught fish were placed in the tank and fed 800 grams of chopped clams
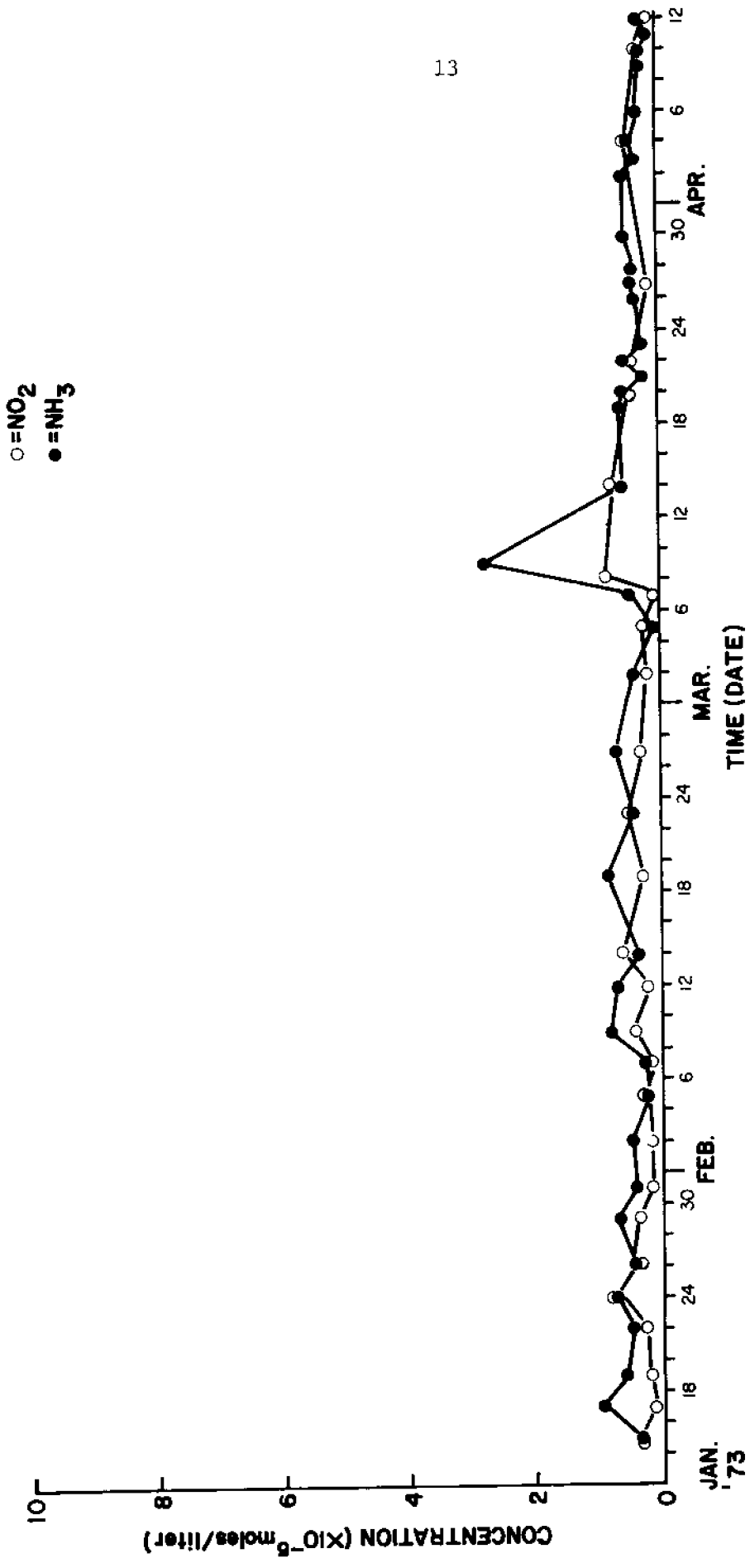
TABLE 4

PRECISION AND ACCURACY OF THE METHOD
IN SEA WATER AT 32 PPT

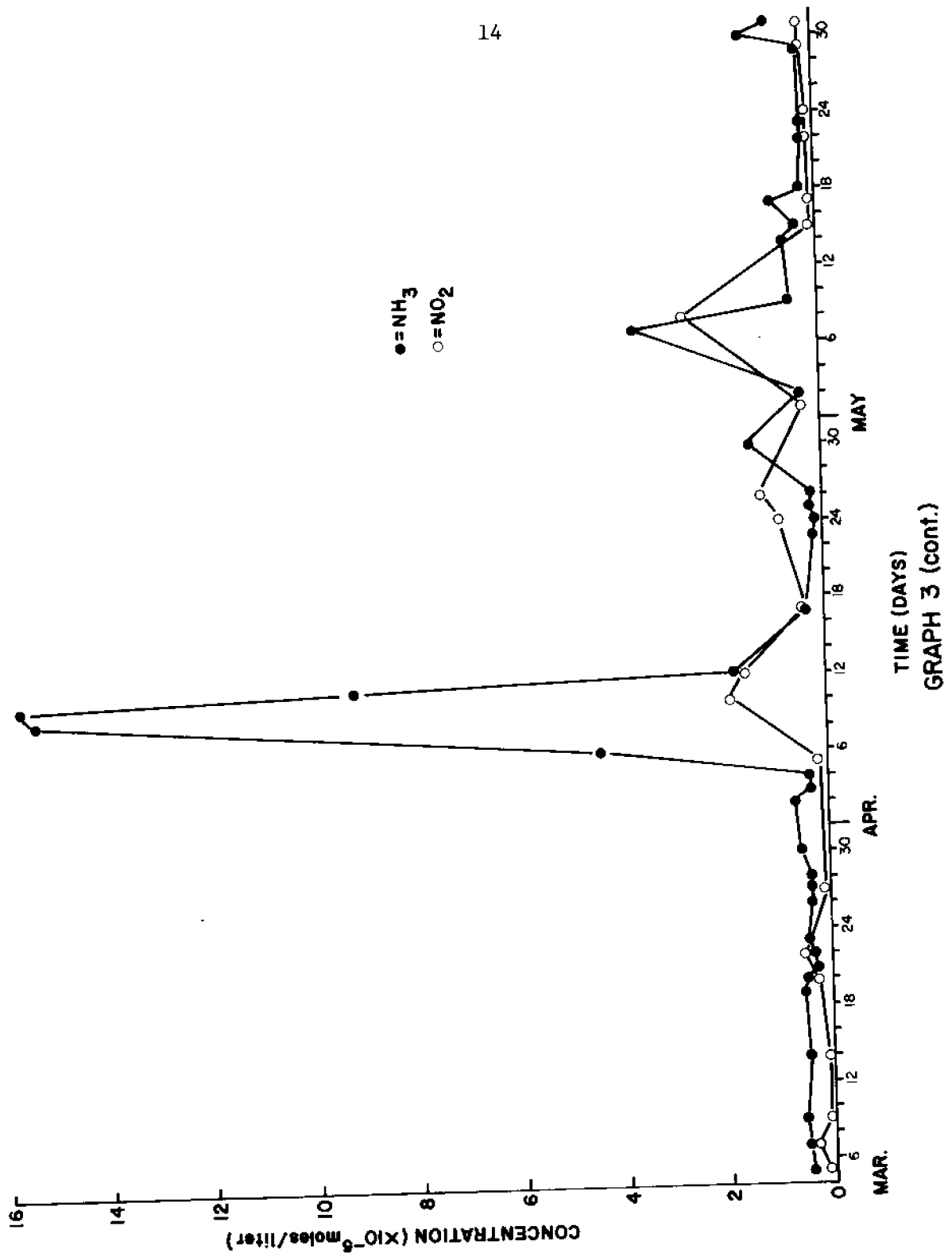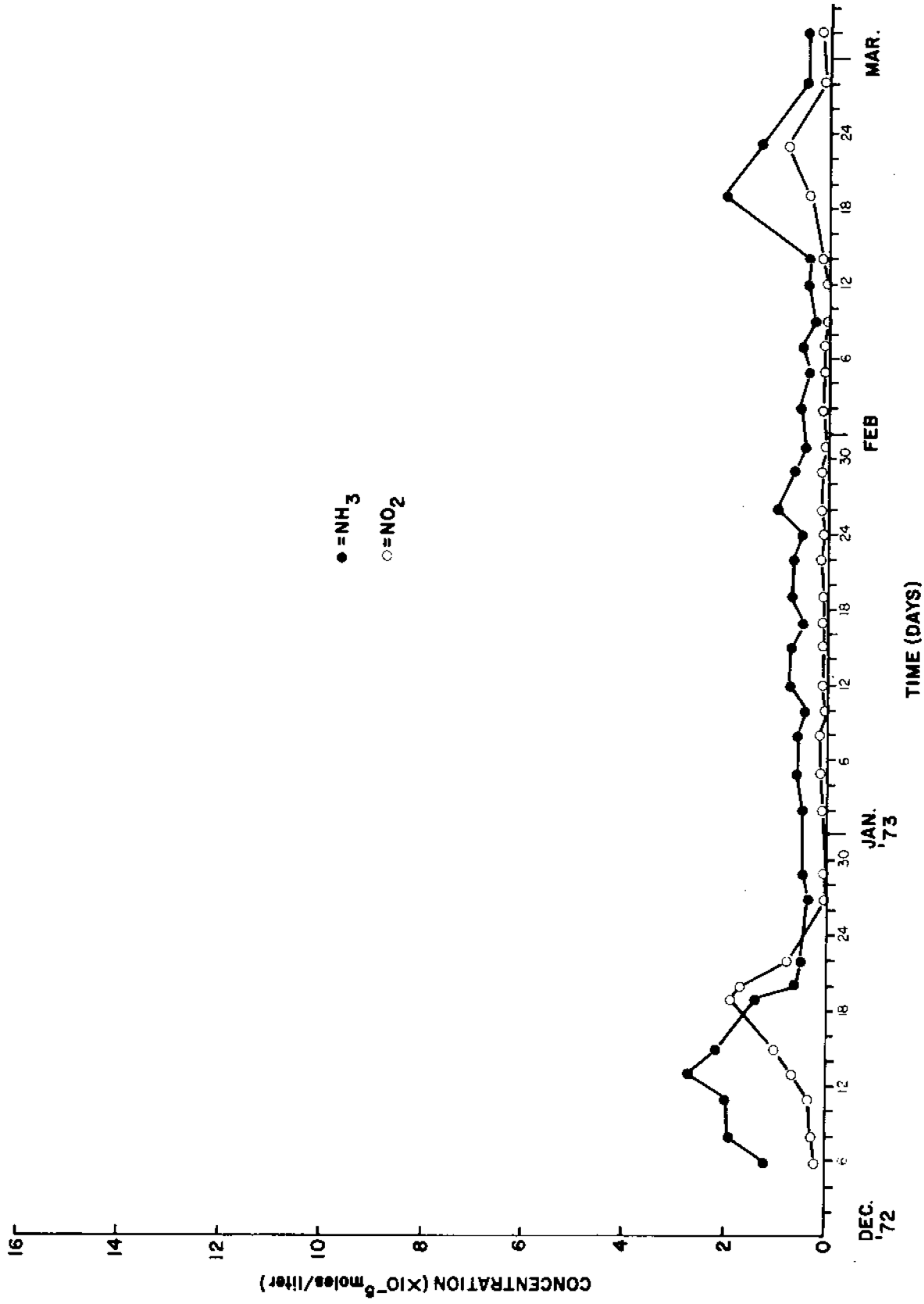| AMMONIA CONCENTRATION Moles/liter	AVERAGE	STANDARD DEVIATION	NUMBER OF REPLICATES
1.00×10^{-6}	$.90 \times 10^{-6}$	.05	8
1.00×10^{-5}	$.97 \times 10^{-5}$	.07	8
1.00×10^{-4}	1.03×10^{-4}	.02	8
1.00×10^{-3}	1.03×10^{-3}	.02	8
1.00×10^{-2}	1.02×10^{-2}	.01	8
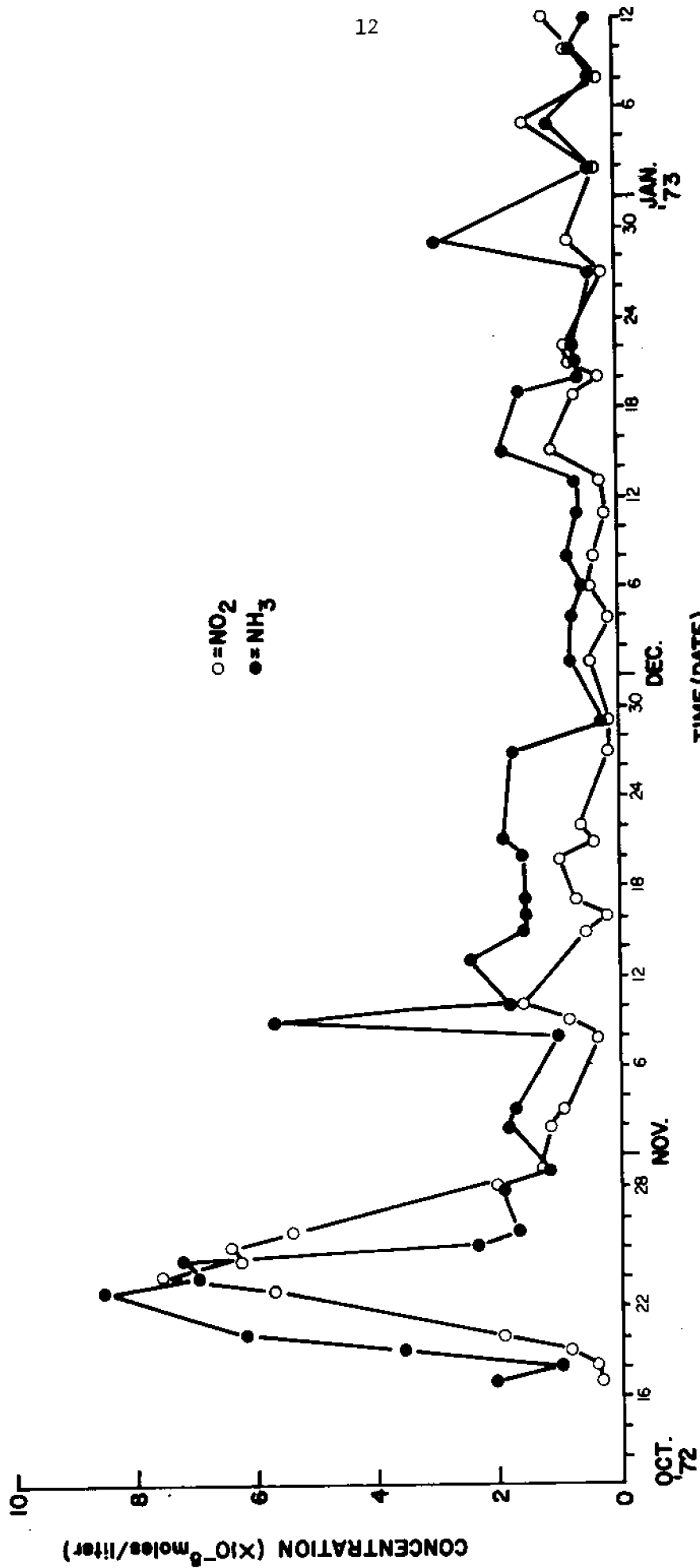
GRAPH 2. Ammonia & Nitrite Concentration in Recirculating System I

GRAPH 2 (cont.)

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GRAPH 3 (cont.)

GRAPH 3. Ammonia and Nitrite Concentration in Recirculating System II.

each day. A more complete description of the facility is given else-where (Epifanio et al., 1973). After the introduction of animals to the system containing a subgravel filter on October 18, an ammonia peak occurred on October 20 and a nitrite peak on October 24. An unexplained shoulder also appears on both the ammonia and nitrite peaks. The data also indicates that daily ammonia monitoring provides reasonable documentation of the filter conditioning process. The behavior of sys-tems containing biological filters during the conditioning process has been reported elsewhere (Spotte, 1970) and the data presented here is consistent with that obtained by others. This system remained quite stable during the rest of the period presented on graph 2 as evidenced by the minor fluctuation in ammonia and nitrite concentrations.

Graph 3 shows ammonia and nitrite levels as recorded for a tank con-taining 2000 adult clams. The tank was similar in design to the one containing local fish. The clams were introduced in lots of 200, 800, and 1000 individuals. Ammonia peaks were recorded after each of the three additions of animals to the system occurring December 5, February 14, and April 4, 1973. These data also suggest that in order to detect significant changes in the ammonia concentration in a recirculating mariculture system, daily ammonia measurements should be made.

Graph 4 shows ammonia and nitrite concentrations measured in a tank through which Delaware Bay water was continuously pumped. The tank con-tained no animal load or biological filter. Clearly the variability of ammonia concentration can be greater in recirculating seawater systems, than in the natural environment.

Graphs 2 and 3 show consistent similarities between the appearance of ammonia peaks and the subsequent appearance of nitrite peaks. The ammonia concentration represents a pivotal variable in the sense that it is produced by shellfish as a waste product and serves as a nutrient source for nitrifying bacteria in the biological filter. The level of ammonia in solution in influenced by changes in the nitrifying bacteria population, by decaying animal meat and by changes in the animal load being serviced by the biological filter. The ammonia concentration in a recirculating system shows a rapid response to system perturbations and a predictable recovery pattern. These facts suggest that routine measurement of ammonia levels and only periodic measurement of nitrite concentration in response to ammonia level fluctuations is adequate for accurate monitoring of a recirculatory mariculture system employing a biological filter.

CONCLUSIONS

The ammonia electrode was tested and characterized for use in monitoring water quality and biological activity in a closed cycle system. Its precision and ease of use make it possible for the ammonia level in the system to be monitored routinely and the ammonia concentration used as a master variable, to detect rapid system changes involving both physical and biological perturbations.

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● = NH₃
○ = NO₂

CONCENTRATION ($\times 10^{-6}$ moles/liter)

10 8 6 4 2 0

OCT. '72   NOV.   DEC.   JAN. '73
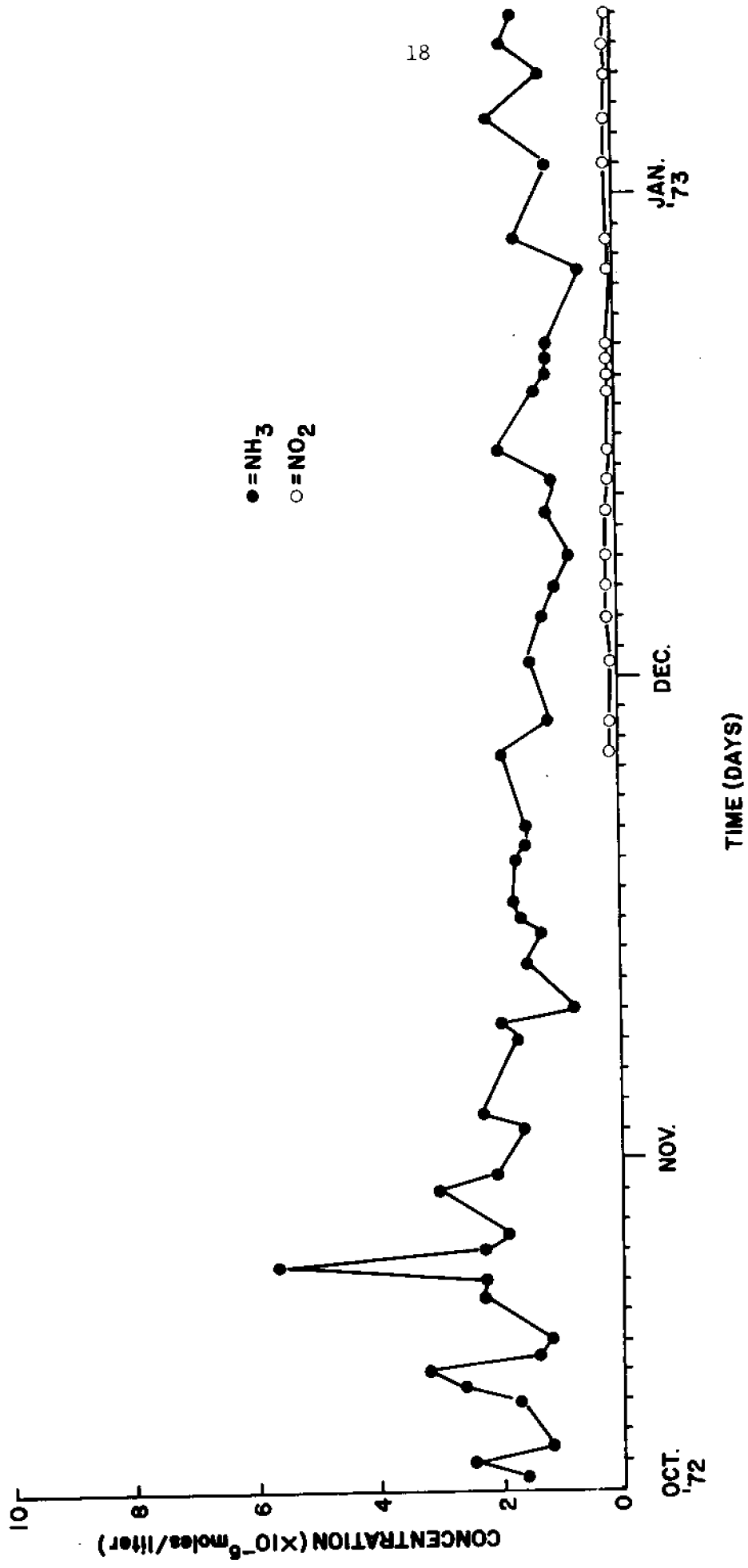
TIME (DAYS)

GRAPH 4. Ammonia and Nitrite Concentration in Tank containing Flowthrough Delaware Bay Water.
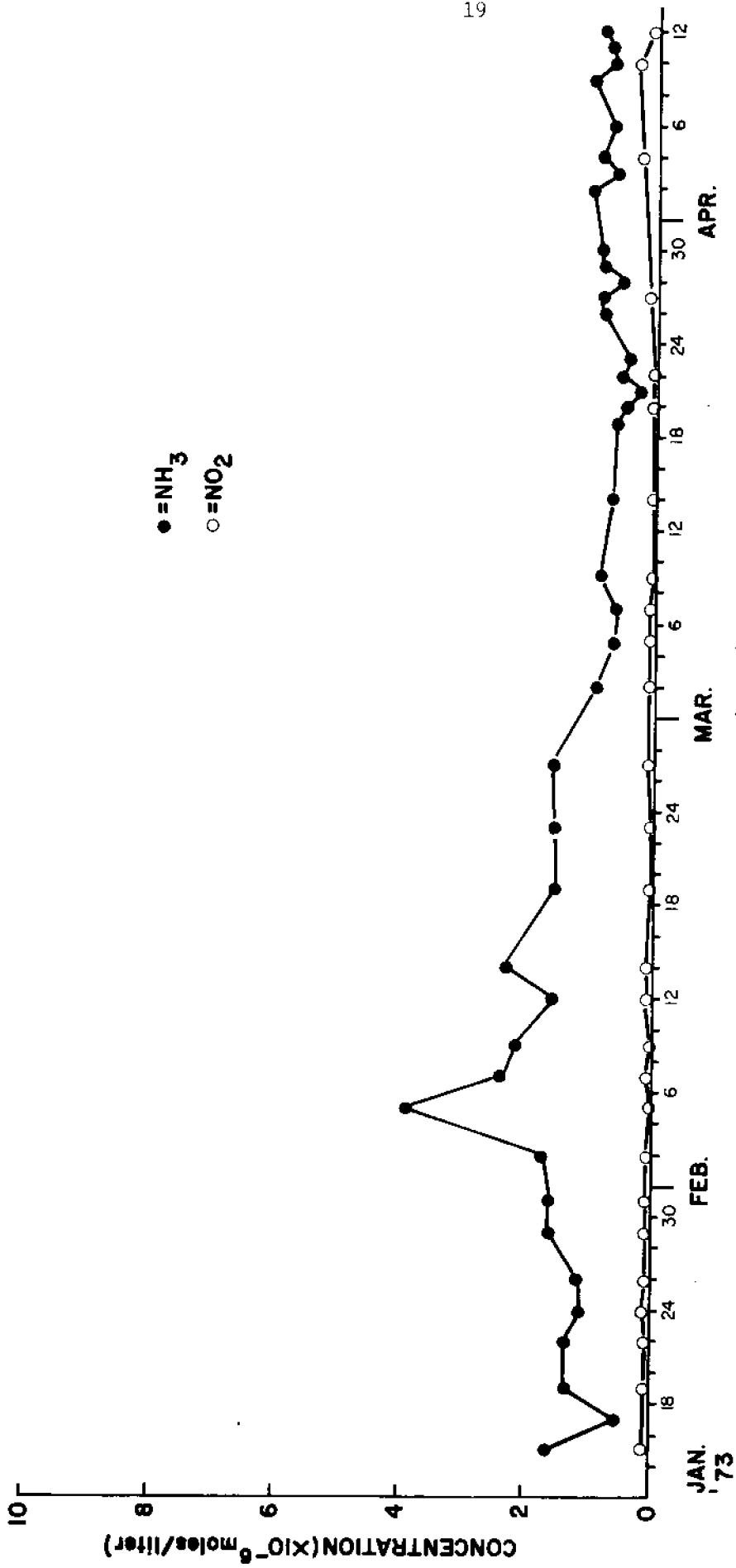
GRAPH 4 (cont.)

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