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The Elimination of Fluctuations During the Use of a Nitrate Specific Ion Electrode

Linda L. Blaine and Frank R. Toman
Department of Biology, Western Kentucky University, Bowling Green, Kentucky 42101

Abstract

Fluctuations in millivolt readings were found to occur when using an Orion nitrate specific ion electrode to measure nitrate concentration.

Those fluctuations were greatest in the weaker nitrate solutions (10^{-4} M and 5×10^{-4} M) and were more pronounced when the electrode had not been renewed for a while. The fluctuations could be reduced greatly if the electrode was preequilibrated in sodium nitrate solution for 0.5 hour with stirring before taking the readings.

Introduction

During experiments in which a nitrate specific ion electrode was used to measure nitrate concentrations, it was observed that millivolt readings for standard sodium nitrate solutions sometimes varied considerably. It was not known if that type of fluctuation varied with the length of time since electrode renewal or if it was a characteristic of all nitrate electrodes. Millivolt readings have an inverse relationship with nitrate concentration. The present study was undertaken to evaluate the precision of the nitrate electrode and to determine the conditions of use under which reproducible results could be obtained.

Materials and Methods

The nitrate specific ion electrode, Orion Model 92-07, was the subject of this study. The reference electrode was a single junction reference electrode, Orion Model 90-01. The electrodes were used in a Corning Model 12 research pH meter.

Dioxane, sodium nitrate, and potassium chloride were of reagent grade. Liquid ion exchanger, 92-07-02, and internal filling solution, 92-07-03, were from Orion Research. Phenyl mercuric acetate was obtained from Eastman Kodak.

Sodium nitrate was used to prepare a 1.0 M solution. The reference electrode was kept filled with 0.1 M potassium chloride. Preservative was prepared by dissolving 0.1 g of phenyl mercuric acetate in 20 ml of dioxane, then diluting to 100 ml with distilled deionized water.

Standards were prepared daily by making dilutions of the 1.0 M sodium nitrate stock solution with glass distilled deionized water. Experiments were run utilizing the following 5 sodium nitrate standards: 10^{-4} M, 5×10^{-4} M, 10^{-3} M, 5×10^{-3} M, and 10^{-2} M. One ml of preservative was added to each liter of distilled deionized water used to prepare standards.

Nitrate electrodes were renewed according to instructions in the Orion Nitrate Ion Electrode Manual (1970).

Four separate experiments were designed to evaluate the electrodes under study and to attempt to obtain reproducible results: (1) no pretreatment of the nitrate electrode, (2) electrodes were rinsed and dried, then immersed in dilute nitrate solution, the switch turned on, and preequilibrated for 0.5 or 1 hour, (3) electrodes renewed on the day prior to use, then preequilibrated for 0.5 hour without stirring and preequilibrated 0.5 hour with stirring, and (4) sensitivities of 3 different nitrate specific ion electrodes were compared; each had been renewed prior to the experiment.

Results and Discussion

Experiment 1—No Pretreatment of Nitrate Electrode

The 5 sodium nitrate standards were read on 5 different days from weakest to

strongest and repeated until reproducible results were obtained (Table 1, Column 1). This required from 45 min to 1 hour each day. The values in the table are the differences in readings for a particular standard between the first and last reading and are the averages for 5 trials on 5 different days. Actual readings ranged from 163 millivolts (mv) to 40 mv on the 10^{-2} M standard. On each day, readings decreased as the standards were read repeatedly. The lower readings indicated that the electrode possessed greater sensitivity after being used for a period of time.

From the results of this experiment, it was decided to test electrodes after they had been preequilibrated for 0.5- and 1-hour periods.

Experiment 2—Pretreatment of the Nitrate Electrode: 0.5 Hour vs. 1 Hour Preequilibration

After the electrodes were rinsed and dried and preequilibrated for 0.5 hour or 1 hour, the nitrate standards were read in the same manner as described for Experiment 1 (Table 1, Columns 2, 3). The values in each column are averages for 4 trials on 4 different days.

Preequilibration for 0.5 hour reduced the amount of total change from the first to the last reading when compared to readings with no treatment. Preequilibration for 1 hour was of very little or no greater benefit than preequilibration for 0.5 hour.

Experiment 3—Pretreatment of a Recently Renewed Electrode: 0.5 Hour Preequilibration vs. 0.5 Hour Preequilibration with Stirring

On the day prior to the beginning of this experiment, the electrode was renewed to determine the stability of readings during the first hour of use following renewal. Nitrate standards were read on 9 different days. On 3 days, the electrode received no pretreatment, and on 3 days, the electrode received 30 min preequilibration as described in Experiment 2. On the other 3 days, the electrode received the same type of pretreatment with the dilute nitrate solution kept in motion with a magnetic stirrer (Table 2). Values for each column are averages for 3 trials.

TABLE 1.—DIFFERENCES IN MILLIVOLTS BETWEEN THE FIRST AND THE LAST READING OF STANDARD SOLUTIONS

Conc.	No preequilibration	0.5 hour preequilibration	1 hour preequilibration
1×10^{-4} M	4.5	2.9	3.1
5×10^{-4} M	2.7	2.0	1.5
1×10^{-3} M	2.1	1.6	1.1
5×10^{-3} M	2.5	1.6	1.5
1×10^{-2} M	2.3	1.4	1.1

This experiment generally showed less change in readings under conditions of no pretreatment when the nitrate electrode had been recently renewed than it did in earlier experiments when it had not been recently renewed (Table 2, Column 1; Table 1, Column 1). The same general trend is indicated when changes in readings after the electrode had been equilibrated for 0.5 hour are compared for recently renewed and not recently renewed electrodes (Table 2, Column 2; Table 1, Column 2). There still remained, however, less change in readings after a 0.5-hour preequilibration period than with no pretreatment in the renewed electrode (Table 2, Columns 1, 2). This further substantiates the need for preequilibration before using the nitrate electrode. The preequilibration apparently is even more important as the electrode ages.

The data reported in Table 2, Column 3, when the electrode was preequilibrated in a dilute nitrate solution kept in motion with a magnetic stirrer, showed less change than with no pretreatment or with 0.5 hour pretreatment with no stirring (Table 2). This indicated that not only is preequilibration important, but that stirring increased the effectiveness of the equilibration period. It should be noted that most of the change in readings during the first week of use after renewal was in the weaker solutions, 10^{-4} M and 5×10^{-4} M (Table 2).

TABLE 2.—DIFFERENCES IN MILLIVOLTS BETWEEN THE FIRST AND THE LAST READING OF STANDARD SOLUTIONS DETERMINED ON A RECENTLY RENEWED ELECTRODE

Conc.	No pre-treatment	0.5-hour pretreatment	0.5-hour pretreatment with stirring
1×10^{-4} M	4.3	2.0	1.1
5×10^{-4} M	1.5	0.3	0.5
1×10^{-3} M	0.7	0.8	0.3
5×10^{-3} M	0.7	1.0	0.3
1×10^{-2} M	0.7	0.5	0.3

Experiment 4—Comparison of 3 Different Nitrate Ion Electrodes

The original Orion nitrate specific ion electrode and 2 other electrodes borrowed from other university departments were renewed before the experiment was begun. Readings were recorded on 6 different days for each electrode, on 3 days, 30-min pre-equilibration with the magnetic stirrer, and 3 days with no pretreatment. The electrodes from the Departments of Agriculture, Biology, and Chemistry, are referred to as Electrodes A, B, and C, respectively (Tables 3, 4). Values are averages for 3 trials on 3 different days.

Previous results with Electrode B showed changes in values during the first half hour of use, and continued in this experiment (Tables 3, 4). The same trend was demonstrated by the other 2 electrodes. Apparently, fluctuations during the first half hour of use are characteristic of all Orion nitrate specific ion electrodes.

TABLE 3.—DIFFERENCES IN MILLIVOLTS BETWEEN THE FIRST AND THE LAST READING OF STANDARD SOLUTIONS DETERMINED ON 3 DIFFERENT ELECTRODES UTILIZING A 0.5-HOUR PREEQULILBRATION PERIOD WITH STIRRING

Conc.	Electrode A	Electrode B	Electrode C
1×10^{-4} M	2.8	4.1	1.5
5×10^{-4} M	0.5	2.1	0.7
1×10^{-3} M	0.8	1.0	0.7
5×10^{-3} M	0.7	0.3	0.5
1×10^{-2} M	0.3	0.5	0.7

TABLE 4.—DIFFERENCES IN MILLIVOLTS BETWEEN THE FIRST AND THE LAST READING OF STANDARD SOLUTIONS DETERMINED ON 3 DIFFERENT ELECTRODES WITH NO PRETREAMENT

Conc.	Electrode A	Electrode B	Electrode C
1×10^{-4} M	3.1	5.8	1.8
5×10^{-4} M	1.3	3.8	1.8
1×10^{-3} M	0.7	2.7	1.7
5×10^{-3} M	0.5	2.0	1.3
1×10^{-2} M	0.5	1.3	1.1

Experiment 4 also showed that changes in behavior of a nitrate ion electrode can be expected between 2 and 4 weeks after being renewed, and is in agreement with an evaluation of the nitrate electrode by Potterton and Schuts (1967). The experiment showed, however, that when working with dilute nitrate solutions, a freshly renewed electrode does not assure that reproducible results will be achieved. In all cases, changes greater than 1.0 mv were obtained with a freshly renewed electrode with no pretreatment when working with solutions of 10^{-4} M concentration (Table 4). Pretreatment with a stirred solution of sodium nitrate reduced changes, but some change in readings was still observed. Thus, the nitrate electrode, when freshly renewed and pretreated as described above, did not give reproducible results for solutions of 10^{-4} M concentration. In all cases, however, reproducible results were obtained eventually for the dilute solutions after the electrode had been in use for about 0.5 hour.

A recently renewed nitrate electrode, when used with more concentrated solutions (10^{-3} M to 10^{-2} M), did not show the variation that exists with dilute solutions (Tables 3, 4). Variations occurred for the more concentrated solutions when the electrode had aged. For Electrode B, greater variation occurred about a month after renewal, and the variation was much more pronounced when the electrode had not been pretreated. There were no millivolt variations after the electrode had been in use for approximately 0.5 hour.

Millivolt readings for nitrate solutions of

10^{-4} M and 5×10^{-4} M with Electrode B, pretreated or not, showed a greater percentage variation than with more concentrated solutions. Even for the lower concentrations, since readings did eventually become reproducible, there was no indication that the electrode failed to give dependable readings when proper technique was utilized as long as 4 to 6 weeks after renewal.

CONCLUSIONS

Experimental results with an Orion nitrate specific ion electrode indicated that millivolt readings decreased during the first half hour of use. Pretreatment by soaking the electrode in dilute nitrate solutions for 0.5 hour reduced but did not eliminate the variation in readings. Preequilibration for 1 hour was of little more benefit than a half hour, but stirring the solution during pretreatment increased the effectiveness.

There was less variation in readings during the first half hour of use when the nitrate electrode had been renewed recently. Variation was further decreased by use of a half-hour preequilibration with stirring. Change in readings was minimal in the stronger nitrate solutions (10^{-2} M to 10^{-3} M), particularly if the fresh electrode was preequilibrated. Weaker nitrate solutions consistently showed greater variations than stronger solutions. For all concentrations, greater variation occurred in readings as the electrode aged. In all cases, readings became reproducible after the electrode had been in use for approximately 0.5 hour.

Comparison of 3 different electrodes indicated that all Orion nitrate specific ion electrodes give similar results when tested under similar conditions. Regardless of factors such as length of time since renewal or nitrate solution concentration, maximum reliability in the electrode is obtained by reading aliquots of a dilute nitrate solution for at least 0.5 hour and determining that stability had been reached prior to making the determinations.

LITERATURE CITED

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