AUTOMATED POTENTIOMETRIC TECHNIQUES FOR THE ON-SITE MONITORING OF

IONS IMPORTANT IN WATER QUALITY CONTROL

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ABSTRACT

The characteristics of the nitrate electrode - fluoride electrode cell without liquid junction were investigated for applicability to nitrate ion analysis. In addition to enabling accurate nitrate analysis, the cell was found to be useful for examining the effects of interfering ions. An attempt was made to use the nitrate electrode in following nitrate ion uptake by algal cultures. The algae interfere to a certain extent with the electrode response. Using knowledge gained from research under this grant, a potentiometric nitrate analysis capability has been set up at the new University of Missouri Environmental Trace Substances Laboratory.

KEYWORDS - electrodes/ ions/ analytical techniques/ nitrates/ fluorides/ algae/ volumetric analysis/ water analysis/ water chemistry

Introduction and Objectives

Since 1966 a number of non-glass ion-selective electrodes utilizing entirely new concepts have been marketed for the potent-iometric analysis of several ions which previously could not be measured by potentiometry. Several of these electrodes are select-ive for ions, e.g., fluoride, nitrate and calcium, which are deeply involved in water quality studies. Since potentiometry as an analytical technique offers numerous advantages in terms of speed, minimal sample preparation, simplicity and adaptability to auto-mated or on-site analysis, there has been a great deal of interest in applying the new ion-selective electrodes to water analysis. As with all new instruments, however, ion-selective electrodes do not do all that the manufacturers claim and require a great deal of technique development before being applied to the analysis of genuine water samples. The purpose of this research, therefore, has been the development of potentiometric techniques using non-glass ion-selective electrodes for the analysis of ions in natural water systems.

The original objectives of the resarch project were (1) the development of a multi-sensor analysis system in which the concen-tration of the desired ion is measured potentiometrically and is automatically corrected for temperature, ionic strength, pH and the presence of interfering ions; (2) the development of a stan-dard addition technique applicable to ion-selective electrodes for the accurate determination of ions present at low concentrations and in the presence of interfering ions; (3) the development of

stable, low-leakage, low-drift reference electrodes for use with ion-selective electrodes; and (4) the development of a flow titration technique for use in automated systems of ion analysis.

Degree of Achievement of Original Objectives

Work on the development of a multi-sensor analysis system was not pursued to any large extent because standard addition techniques appear to be much more satisfactory.

Further work was continued on standard addition methods for the analysis of ions. Basically the standard addition technique consists of (1) recording the potential of the electrode system in an accurately measured volume of the unknown solution, (2) adding a small volume of a relatively concentrated standard solution of the ion being measured, (3) recording the change in potential resulting from the addition of standard and (4) calculating the concentration of unknown ion by the appropriate mathematical calculations. This approach gives much more accurate analyses than direct potentiometry.

Approaches attempted on the development of low-leakage, low-drift reference electrodes were unsuccessful due to the excessively high junction potentials which resulted.

Because of the superior accuracy of the standard addition technique, work was not continued on the development of a flow titration method.

Research Procedures and Results

Attempts were made to evaluate the effects of interfering ions at the nitrate electrode by using the following cell:

$$\text{fluoride electrode} \mid F^-, \ NO_3^- \mid \text{nitrate electrode}$$

This electrode system was developed and found to be highly
advantageous for nitrate analysis under Project No. B-023-Mo,
"Automated Potentiometric Techniques for the On-Site Monitoring
of Anion Concentrations in Water". Typically the inital solution
consists of 100 ml containing nitrate at the desired concentration
and containing a low concentration of fluoride (ca. 1×10^{-4} M) to
poise the potential of the fluoride electrode. The potential of
the electrode system is given by Equation 1.

$$E_1 = E_a - \frac{2.3RT}{F} \log \frac{\gamma_n [NO_3^-]}{\gamma_f [F^-]} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 1$$

In Equation 1, E_1 is the initial potential, E_a is a constant for
the electrode system in question, $\frac{2.3RT}{F}$ is the Nernstian slope,
γ_n is the initial single ion activity coefficient of nitrate ion,
γ_f is the single ion activity coefficient of fluoride ion, $[NO_3^-]$ is
the initial concentration of nitrate ion and $[F^-]$ is the initial
concentration of fluoride ion. As an example assume that the inter-
fering ion being studied is iodide ion. To V ml of NO_3^--F^- solution,
add v ml of stock solution of interfering iodide of concentration, S,
such that the potential shifts negative by no more than a few mv.
The new potential, E_2, is given by

$$E_2 = E_a - \frac{2.3RT}{F} \log \frac{\gamma_n' [NO_3^-]\frac{V}{V+v} + K \gamma_{iV}' \frac{Sv}{V+v}}{\gamma_f' [F^-]\frac{V}{V+v}} \quad \dots\dots\dots\dots\dots\dots 2$$

where the activity coefficients are designated by primes to indi-
cate that they may have in fact changed somewhat by the addition

of interfering ion. Assuming that the ratios of the activity coefficients do not change, i.e.,

$$\gamma_n / \gamma_f = \gamma_n' / \gamma_f' \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 3$$

it can be shown that:

$$Z = \text{antilog} \left| \frac{E_2 - E_1}{-\frac{2.3RT}{F}} \right| = \frac{[NO_3^-] + K \frac{\gamma_1'}{\gamma_n'} \frac{Sv}{V}}{[NO_3^-]} \quad \dots\dots\dots\dots\dots\dots 4$$

The value of K may be evaluated from a plot of $Z - 1$ vs. $\frac{\gamma_1'}{\gamma_n} v$

according to the following equation:

$$Z - 1 = \frac{S}{[NO_3^-] V} K \times \frac{\gamma_1'}{\gamma_n} v \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 5$$

In the equations above K is the selectivity ratio of the interfering ion; the higher its magnitude, the greater the interference. Of more practical utility, a conditional selectivity ratio, K', may be defined as

$$K' = K \frac{\gamma_1'}{\gamma_n} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 6$$

and may be evaluated from Equation 7:

$$Z - 1 = \frac{S}{[NO_3^-] V} K' v \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 7$$

Attempts were made to use the approach outlined above with iodide ion, chloride ion, sulfate ion and bromide ion as interferences. Despite the high stability of the electrode system, the results were not reproducible leading to the belief that the basic theory of interfering ions does not apply to liquid ion exchanger electrodes such as the nitrate electrode. Work is being continued in the area and it is hoped that meaningful results may be reported soon.

Under a previous grant, Project No. B-023-Mo, the nitrate
ion-selective electrode was utilized to follow the reduction
of nitrate to nitrite by a species of bacteria which had that
capability. It was found that the electrode was in fact cap-
able of following the kinetics of the reaction. The electrode
function did not appear to be seriously hampered by the presence
of the bacteria, nor did the contact of liquid ion exchanger of
the electrode appear to have any adverse effect upon the bacteria.
One problem, however, was that the electrode responds to a certain
extent to the nitrite formed in the reaction, which causes error
and necessitates a correction.

Some preliminary efforts were made to extend the work by
using the nitrate electrode to follow the uptake of nitrate by
a heavy suspension of chlorella algae. Besides the fundamental
importance of the experiment, it was felt that the system might
be more satisfactory than the bacterial suspension because there
would be little intermediate formation of nitrite and, therefore,
no nitrite interference. It was found, however, that the electrode
response in the chlorella suspension was very erratic with severe
drifting. Furthermore, immersion in the algal medium for any
appreciable length of time resulted in irreversible damage to the
electrode membrane and necessitated rebuilding.

Using techniques developed under this grant a standard nitrate
analysis method was written up for use in the University of Missouri
Environmental Trace Substances Laboratory. A copy of the procedure
used in the Laboratory follows:

ENVIRONMENTAL TRACE SUBSTANCES CENTER
University of Missouri

Method of Analysis: Nitrates in Water

Instrumentation

The equipment used for the analysis of nitrates in water
consists of the Orion Model 801 digital pH meter, an Orion Model
92-07 nitrate electrode and the Orion Model 90-01 single junction
reference electrode. Important - the filling solution provided
with the single junction reference electrode contains a high con-
centration of nitrate ion and cannot be used for nitrate analysis.
The reference electrode must be filled with 0.01 molar KCl saturated
with AgCl and containing approximately one drop per liter of Triton-
X-100 surfactant as a wetting agent. Higher concentrations of KCl
should not be used because leakage of chloride into the system may
cause interference at the nitrate electrode. In addition, a magnetic
stirrer is required to stir the solutions at a constant rate.
Electrode potential varies somewhat with stirring rate, so a con-
stant, regular rate of stirring is required. To prevent heating of
the solution by the stirring motor, the beaker should be insulated
from the stirrer surface. The bottom of a disposable polystyrene
coffee cup serves very well for that purpose.

Samples

A sample of 100 ml is most convenient, although as little as
25 ml may be analyzed. Since nitrate is subject to microbial action,
the samples should be cooled to ice temperature as soon as possible
after collection and refrigerated, or preferably frozen. Freezing
has the additional advantage of precipitating out calcium salts
which might cause some interference. The only common preservative
which the nitrate electrode is known to tolerate is toluene. Mercury
salts or sulfuric acid may not be used. Prior to analysis the sample
must be heated to 23-27°C.

Calibration Curve

Over the concentration range 1×10^{-5} - 1×10^{-1} $\underline{M}$ the nitrate electrode responds to nitrate ion in a Nernstian-like manner according to the equation

(1) $E = E_a - S \times \log[NO_3^-]$

where E is the measured potential, E_a is a constant (which, however, varies with a number of factors) and S is the slope which has a value of 55 - 60 mv depending upon nitrate ion concentration, temperature and electrode condition.

Calibration plots of E $\underline{vs.}$ $\log[NO_3^-]$ should be prepared frequently, i.e., at least once each week, each time the electrode is rebuilt or whenever there is any suspicion of electrode malfunction. The calibration plot is most conveniently prepared as follows:

A. Place the electrode system in 100.0 ml of water stirred evenly with a magnectic stirrer.

B. From 10 ml microburet add 1.00 ml of 1.00×10^{-3} $\underline{M}$ KNO_3 and allow the system to come to equilibrium for 10-15 minutes.

C. Add accurately measured volumes of standard nitrate solutions of increasing concentrations such that the amount of nitrate added each time is doubled ($\Delta E = \underline{ca.}$ -18 mv for each addition) until the total nitrate concentration reaches 1.00×10^{-2} $\underline{M}$.

D. Calculate $[NO_3^-]$ after each addition taking into account dilution and plot E $\underline{vs.}$ $[NO_3^-]$ on one-cycle, semi-log paper. At least three plots will be required to cover the range, but greater accuracy will be obtained by spreading out the concentration scale. If the slope of the plot is not in the range -58.0 to -59.5 mv/decade at the 2×10^{-4} $\underline{M}$ nitrate level, a calculation error or electrode malfunction should be suspected.

Nitrate Analysis, Comparison to a Standard Solution

A. Measure the potential, E_s, of the electrode system in a standard solution 1.000×10^{-4} $\underline{M}$ in KNO_3.

B. Measure the potential, E_u, of the unknown solution.

C. From the calibration curve find the concentration corresponding to $E_u - E_s$ comparing to the potential at 1.000×10^{-4} $\underline{M}$ nitrate. For example, if $E_u - E_s = -12.5$ mv, go 12.5 mv negative from the potential of the 1.000×10^{-4} $\underline{M}$ point on the calibration curve and read the concentration of nitrate on the concentration axis. The greater the magnitude of $E_u - E_s$, the less the accuracy of the procedure. If $E_u - E_s$ exceeds ± 30 mv, another standard closer to the unknown in concentration should be chosen and the procedure repeated. Results from this procedure ordinarily have a relative accuracy ranging from $\pm 10\%$ at the lower level to $\pm 5\%$ above $\underline{ca}$. 2×10^{-4} M.

Nitrate Analysis, Standard Addition

Potentiometric standard addition analysis is inherently more accurate than direct comparison to a standard and is the preferred technique.

A. With a volumetric pipet place 100.0 ml of sample in a 150 ml beaker, immerse the electrode system and allow equilibration to occur. The potential of the electrode system compared to a previously determined calibration curve will give the approximate value of the concentration of nitrate ion.

B. From a 5- or 10-ml microburet add a small volume of a relatively concentrated standard nitrate solution such that the potential of the electrode system is shifted negative by 12 -18 mv.

C. Calculate the unknown concentration of nitrate ion from the formula

$$(2) \quad \text{antilog} \frac{\Delta E}{-S} = \frac{\dfrac{[NO_3^-]V}{V + v} + \dfrac{Cv}{V + v}}{[NO_3^-]}$$

where ΔE = the shift in potential, V = the volume of unknown, v = the volume of standard added, C = the concentration of standard, S = the electrode response slope in the concentration range covered and $[NO_3^-]$ = the

original nitrate ion concentration. For even higher
accuracy is needed, a standard addition technique using
the fluoride electrode as a reference may be used.[1]

Troubleshooting

Symptom	Cause
Violent fluctuations in potential	Bubble underneath the nitrate electrode or electrodes not plugged in.
Fluctuation and drift in soil suspensions	Colloidal soil particles or algae. Filtration through millipore filter under pressure (not vaccuum) is recommended.
Slow drift in unknown solution	Interfering ions, check for chloride or sulfate.
Fluctuation of ± several tenths of a millivolt in standard or unknown	Cause not known, but sometimes remedied by the addition of a very small drop of Triton-X-100 surfactant.
Electrode malfunction not remedied by any of the above	Electrode membrane fouled. The electrode should be rebuilt.

(1) Manahan, S.E.: Analytical Chemistry, 42, 128 (1970)

Applications and Relevance to Water Resources Research

The research accomplished under this grant has hopefully advanced the state of the art regarding the application of ion-selective electrodes to water analysis and fundamental water resources research. The new electrodes such as the nitrate electrode and fluoride electrode have already been established as useful tools in the water resources area. New applications undoubtedly will be found for existing electrodes and new electrodes likely will be developed.

The area of ion-selective electrodes, being new and interesting, has been plagued by overly exhuberant claims on the part of manufacturers and some investigators. An attempt has been made in this completion report to point out negative results as well as positive results. Furthermore, in papers presented orally, a point was made regarding the limitations of ion-selective electrodes as well as their capabilities. It is just as essential for a non-chemist to know what an analytical tool will not do as to know what it will do, information not usually available in the scientific literature or from the manufacturers.

The use of the nitrate electrode in algal cultures, although unsuccessful to date, is potentially very useful in fundamental studies of algal growth and eutrophication and is deserving, therefore, of further investigation. It is likely that an apparatus permitting continuous circulation of filtered culture medium (i.e., with cells removed by filtration), would permit continuous nitrate monitoring in such a system.

Publications and Papers Presented

Publications:

1. "Electrochemical Methods," S. E. Manahan, _American Industrial Hygiene Association Journal_, in press.

Papers presented:

1. "Ion-Selective Electrodes in Cells without Liquid Junction," University of Minnesota Department of Chemistry, 1970.

2. "Ion-Specific Electrodes," American Industrial Hygiene Conference, Detroit, Michigan, 1970.

Training Accomplished

Two graudate students have been supported in part on this grant. It is felt that doing research on problems directly relevant to water quality has been a valuable part of the training of these students.

In addition, two analytical chemists at the University of Missouri Environmental Trace Substances Center were trained in the uses of ion-selective electrodes by the principal investigator.