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A Sensitive and Highly Selective Nitrate Ion Selective Electrode from a Pencil Lead: An Analytical Laboratory Experiment

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Introduction

Nitrate (NO_3^-) is an important and commonly occurring nitrogen species in the environment. It is applied in both urban and rural areas as a component of fertilizer, and is a major component of concern in the effluent of wastewater treatment plants. Excess nitrate in freshwater and marine ecosystems can lead to algal blooms and eutrophication (1). When ingested, nitrate is known to be reduced to nitrite which is further converted to N-nitrosamines, which are suspected carcinogens (2). A specific toxic effect of nitrates on infants is called methemoglobinemia, a condition that can result in mental retardation, or even death (3).

Because of its role in ecosystem dynamics, and its potential impact on human health, nitrate levels in water are regulated and carefully monitored in engineered and environmental systems. For example, drinking water from groundwater wells in agricultural regions must be regularly checked for nitrate. There are many methods for measuring aqueous nitrate concentrations, including spectroscopic (4-6), chromatographic (7) and electrochemical (8-9) techniques. Such methods often require expensive equipment, and/or require extensive pre-treatment procedures which may involve the use of other toxic chemicals.

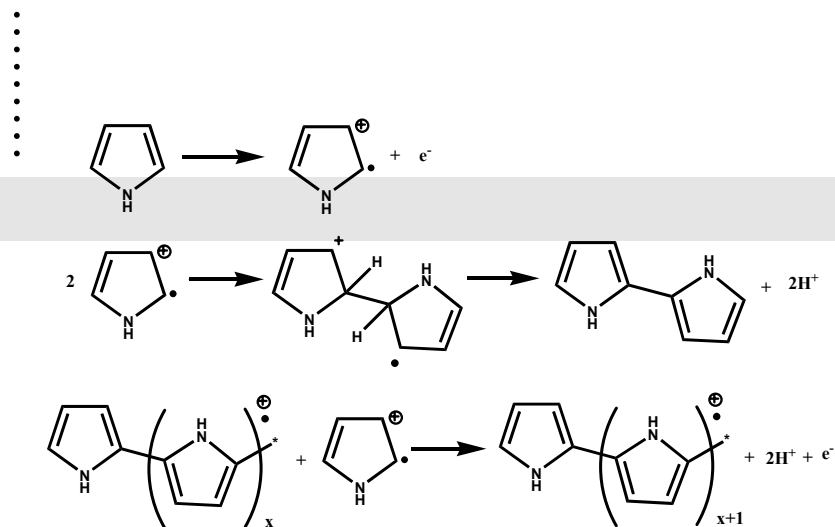
A rapidly developing technique for the rapid determination of the concentration of nitrate other ionic species involves the used of ion selective electrodes (ISE). Despite the promising nature of this technology, many early ISE were found to be insufficiently selective and sensitive for environmental applications. It has recently been shown that doped polypyrrole films can be used as highly selective membranes in ISE fabrication (10-11). When pyrrole is doped with nitrate ions during the polymerization process, a

nitrate-selective ISE can be prepared (12). Electrodes prepared in this manner exhibit several orders of magnitude greater selectivity toward nitrate ions than do commercial analogs, while achieving the same sensitivity (13).

This work summarizes a simple procedure for preparing and testing a nitrate ISE based on doped polypyrrole films. The procedure does not require expensive equipment or extensive sample preparation, and it designed for an upper-level undergraduate laboratory. The procedure over a relatively short period of time (two labs) allows to students to learn the basics of electrochemical polymerization, a potentiometric technique for quantitative analysis and how an ion selective electrode works. In addition, the procedure instills the value of ingenuity by using every day pencil leads as a substitute for expensive glassy carbon electrode substrates (12). Students may be asked to bring different types of pencil leads (manufacturer, softness). During the two lab periods they will have an opportunity to complete all “steps” of the electrode manufacturing process, including preparation of the “electrode body”, deposition of the nitrate-doped polymer layer and electrode testing. In summary, students will experience how to convert a simple pencil lead to a sensitive nitrate ISA.

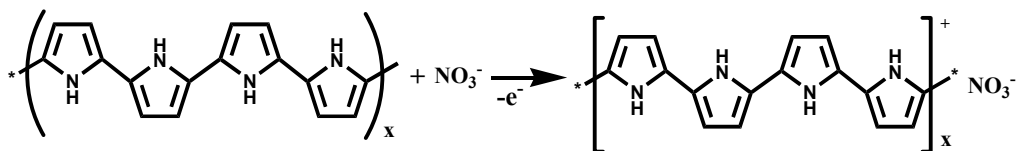
Doped Polypyrrole System

Polypyrrole is one of the most widely studied conducting polymers because of its ease of preparation, high conductivity and relative stability (14). The polymerization process of pyrrole (C_4H_5N) is shown in Scheme I.



Scheme I

In the oxidized state, polypyrrole exist as a polyradical cation, and at the oxidation stage anions (NO_3^- in our case) are attracted electrostatically into the polymerized film as a counter ions (dopant) (15-16) as illustrated in Scheme II.



Scheme II

This particular structure, involving an exchangeable counter ion, has led to the application of polypyrrole as a membrane component for ISEs.

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Potentiometric Measurements with Polypyrrole Doped ISE

Polypyrrole doped electrodes show high selectivity towards the dopant ion. A layer of polypyrrole doped with nitrate is expected to have pores that are complementary to the size of the target ion (NO_3^-). Thus, when expose to a nitrate solution, NO_3^- will move from the region of high nitrate activity to the region of low nitrate activity (from the polymer film to the studied solution or vice versa). As a result a constant potential difference across the interface is formed (eq 1).

$$E = RT / nF \ln(A_{\text{in}}/A_{\text{out}}) \quad (1)$$

R is the gas constant , F is the Faraday constant, T is the temperature, n is the ion charge (in the case of NO_3^- n = 1) and A_{in} and A_{out} are the activities of the NO_3^- ion in the polymer film and in the solution, respectively. Since the concentration of nitrate within the polymer does not change it can be represented as a constant. Converting the natural logarithm in eq 1 to the base 10 logarithm, and inserting $T = 298.15 \text{ K}$ gives the most useful form of the equation, eq 2,

$$E = \text{constant} - \beta (0.059) \log A(\text{NO}_3^-)_{\text{out}} \quad (2)$$

where β is the electromotive efficiency with a value is close to 1 for most electrodes (17).

According to eq 2, potential is expected to change by 59.16 mV for every factor-of-10 difference in nitrate activity.

Experimental Procedure

The experimental procedure is designed for two lab periods. Electrode preparation and doped polypyrrole electrochemical deposition are accomplished in the first period, while electrode testing (determination of nitrate concentration in different samples) is

performed in the second period. All chemicals are commercially available and can be purchased from Aldrich. High resistivity distilled water is required for solution preparation.

Electrodes are prepared from pieces (approximately 2.5 cm) of pencil lead connected to copper wire with another thin and flexible wire as shown in Figure 1. To guarantee a good contact between pencil lead and copper wire, silver paint or another conductive glue can be applied to the connection.

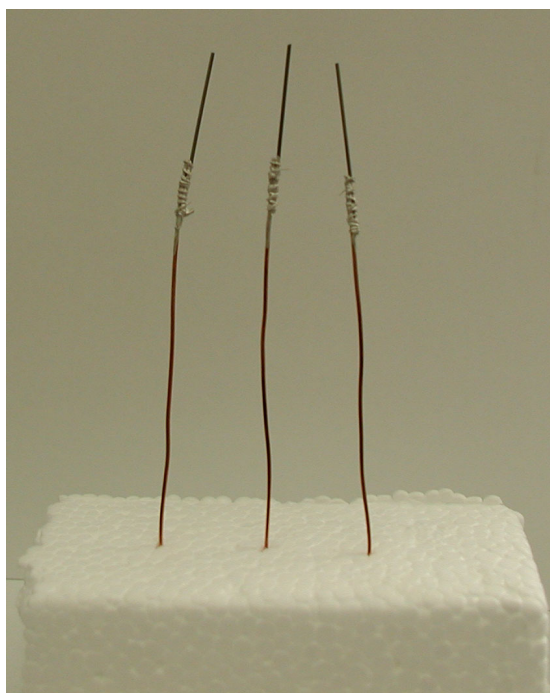


Figure 1: Photograph of three pencil lead electrodes.

No pretreatment of pencil leads (e.g., cleaning or polishing) is required. In our experiments we used the soft kind of lead 2B with 0.5 mm diameter, Shine, Taiwan. A 1.5 cm length of lead was immersed in a pyrrole solution for polypyrrole deposition. Thus, the total exposed (working) surface of the electrode was 0.238 cm^2 .

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Polymerization of pyrrole doped with nitrate onto pencil lead electrodes was performed electrochemically. We prepared electrodes galvanostatically. Princeton

Applied Research Potentiostat/Galvanostat, Model 263A was used to supply constant currents running from 350-650 μA (current densities of $j = I/S = 0.45\text{-}0.65 \text{ mA} / 0.238 \text{ cm}^2 = 1.89 - 2.74 \text{ mA cm}^{-2}$) for 20 minutes. Silver wire/disk electrode and platinum wire/disk electrodes were used as reference and counter electrodes, respectively. The electropolymerization solution consisted of 1 M pyrrole and 0.1 M NaNO_3 . This solution was purged with nitrogen for 5 minutes before deposition to remove oxygen.

After polymerization, electrodes must remain in a $1 \times 10^{-2} \text{ M NaNO}_3$ solution at least 24 hours for conditioning. After that they can be used for potentiometric measurements of nitrate. Potentiometric measurements can be performed with any pH/voltmeter. We used a Ag/AgCl double junction electrode as a reference electrode $1 \times 10^{-2} \text{ M (NH}_4)_2\text{SO}_4$ solution as an ionic strength adjuster (ISA). Between measurements, we store our electrodes in the dark place in a $1 \times 10^{-2} \text{ M NaNO}_3$ solution.

Hazards

There are hazards associated with using pyrrole. Purification of pyrrole and preparation of aqueous pyrrole solution must be performed in a fume hood. To avoid skin contact with pyrrole and other reagents, latex gloves can be used. Excess electropolymerization solution should be disposed of as organic waste.

Results and Discussion

Nitrate doped polypyrrole electrodes were tested potentiometrically for their response to NO_3^- ion two days after deposition. Calibration curves obtained for three electrodes deposited at different current densities ($1.89 - 2.74 \text{ mA cm}^{-2}$) are shown in Figure 2.

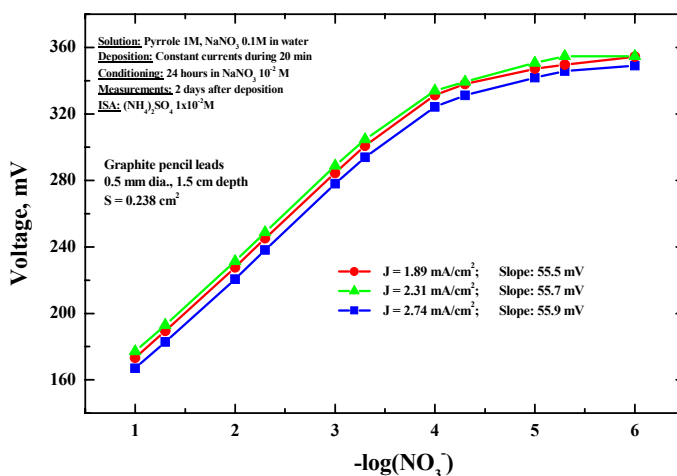


Figure 2. Potentiometric response of polypyrrole electrodes doped with nitrate to NO_3^- ion. Deposition: constant current of $450 \mu\text{A}$ (circle), $550 \mu\text{A}$ (triangle), $650 \mu\text{A}$ (square) were applied during 20 min. Electropolymerization solution: pyrrole 1M and NaNO_3 0.1M. Measurements: at $T = 22 \text{ }^\circ\text{C}$, 2 days after deposition.

All three electrodes exhibited Nernstian behavior (Slopes $55.7 \pm 0.2 \text{ mV}$ per log cycle of nitrate concentration, at $T = 22 \text{ }^\circ\text{C}$), with a linear response to nitrate concentrations spanning four orders of magnitude ($0.1 - 1 \times 10^{-4} \text{ M}$ or $6200 - 6.2 \text{ ppm}$ of NO_3^-) and a detection limit $(2 \pm 1) \times 10^{-5} \text{ M}$ ($1.9 - 0.6 \text{ ppm}$) of nitrate. The detection limit is approximately order of magnitude lower than safe levels of nitrate in drinking water as regulated by the U.S. Environmental Protection Agency EPA (10 ppm) (18) and the European Community (EC) Nitrate Directive (11.3 ppm) (19).

A wide variety of unknowns can be analyzed with this nitrate ISE, including laboratory prepared solutions with different nitrate concentrations, tap water samples or

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samples from environment expected to have nitrates, such as well water in agricultural regions. Any unknowns do not require additional pretreatment before measurements except adding of ionic strength adjuster.

Conclusion

A simple procedure for manufacturing of a sensitive nitrate ISE from pencil lead is proposed. In addition to chemistry educational content, this experiment has enormous pedagogical motivations for students interested in sensor development, micro-fabrication procedures, advanced monitoring of environmental problems and creating solutions to those problems.

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