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A Sensitive Nitrate Ion-Selective Electrode
from a Pencil Lead

An Analytical Laboratory Experiment

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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).

Because of its role in ecosystem dynamics and its potential impact on human health (2, 3), nitrate levels in water are regulated and carefully monitored in engineered and environmental systems. There are many methods for measuring aqueous nitrate concentrations, including spectroscopic (4–6), chromatographic (7), and electrochemical (8, 9) techniques. Such methods often need expensive equipment or require extensive pretreatment procedures that may involve the use of other toxic chemicals.

The use of ion-selective electrodes (ISE) is a rapidly developing technique for the rapid determination of the concentration of nitrate and other ionic species. 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).

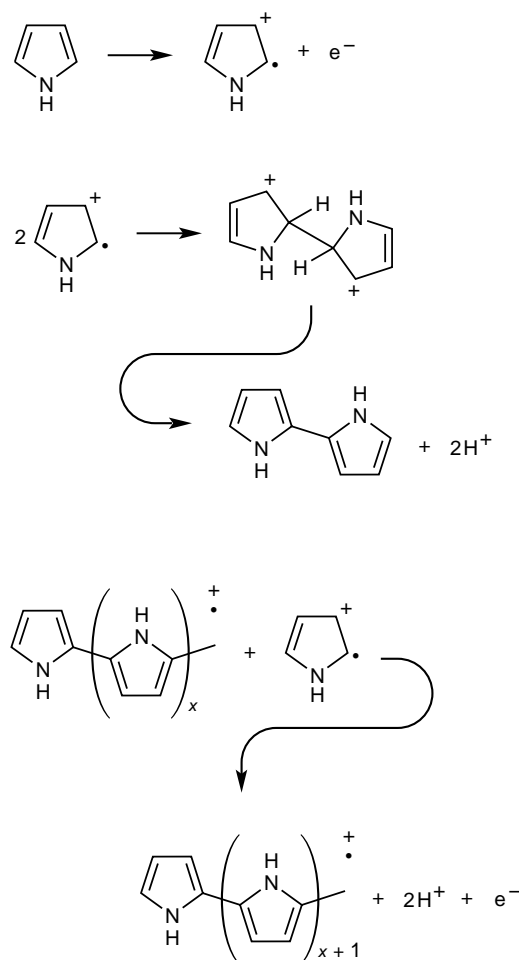
This article summarizes a simple procedure for preparing and testing a nitrate ISE based on doped polypyrrole films. The procedure does not require expensive equipment or extensive sample preparation and is designed for an upper-level undergraduate laboratory. Over a relatively short period of time (two labs), the procedure allows 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 everyday pencil leads as a substitute for expensive glassy carbon electrode substrates. Students may be asked to bring different types of pencil leads (manufacturer, softness). During the two lab periods the students 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 ISE.

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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 ($\text{C}_4\text{H}_5\text{N}$) includes release of two moles of electrons per one mole of pyrrole and is shown in Scheme I.

In the oxidized state polypyrrole exists as a polyradical cation, and at the oxidation stage anions (NO_3^- in our case) are attracted electrostatically into the polymerized film as



Scheme I. The polymerization process of pyrrole ($\text{C}_4\text{H}_5\text{N}$).

counter ions (dopant) (15, 16) as illustrated in Scheme II. This particular structure, involving an exchangeable counter ion, has led to the application of polypyrrole as a membrane component for ISEs.

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 the doped polypyrrole is exposed 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

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

where $R = 8.314510 \text{ V C K}^{-1} \text{ mol}^{-1}$ is the gas constant, $F = 9.6485309 \times 10^4 \text{ C mol}^{-1}$ is the Faraday constant, T is the temperature in K, n is the magnitude of 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

$$E = \text{constant} - \beta(0.05916 \text{ V}) \log A(\text{NO}_3^-)_{\text{out}} \quad (2)$$

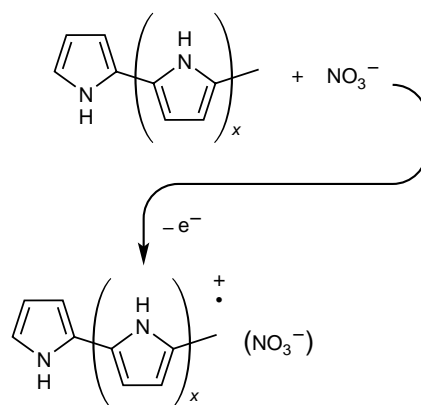
where β is the electromotive efficiency with a value is close to 1 for most electrodes (17). According to eq 2, potential is expected to change by 59.16 mV for every factor-of-10 difference in nitrate activity.

Experimental Procedure

The experimental procedure was designed for two lab periods. Electrode preparation and polypyrrole-doped electrochemical deposition were accomplished in the first period, while electrode testing (determination of nitrate concentration in different samples) was performed in the second period. All chemicals were commercially available and were purchased from Aldrich. High resistivity distilled water was used for solution preparation.

Electrodes were prepared from pieces (approximately 2.5-cm length) 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 other conductive glue was applied to the connection. No pretreatment of the pencil leads (e.g., cleaning or polishing) was required. Soft lead (2B) with a 0.5-mm diameter (Shine, Taiwan) was used. 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 0.24 cm^2 .

Polymerization of pyrrole doped with nitrate onto pencil lead electrodes was performed electrochemically. Electrodes were prepared galvanostatically. A Princeton Applied Research Potentiostat-Galvanostat (Model 263A) was used to supply constant currents running from 450–650 μA (current densities of $j = I/S = 0.45\text{--}0.65 \text{ mA}/0.24 \text{ cm}^2 = 1.89\text{--}2.74 \text{ mA}$



Scheme II. Doping of polypyrrole by nitrate. One unit of charge is spread over four pyrrole units.

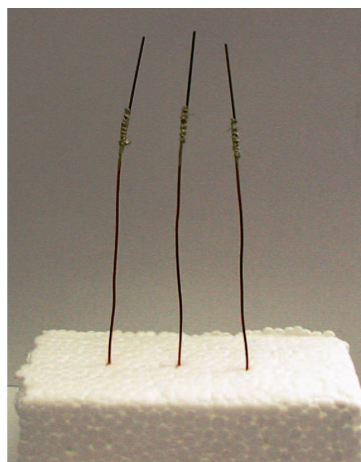


Figure 1. Pencil lead electrodes.

cm^2) for 20 minutes. Silver wire or disk 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 remained in a $1 \times 10^{-2} \text{ M NaNO}_3$ solution for at least 24 hours for conditioning, and were then used for potentiometric measurements of nitrate. Potentiometric measurements can be performed with any pH or voltmeter. A Ag/AgCl double junction electrode was used as a reference electrode and $1 \times 10^{-2} \text{ M } (\text{NH}_4)_2\text{SO}_4$ solution as an ionic strength adjuster (ISA). Between measurements, the electrodes were stored in the dark 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.

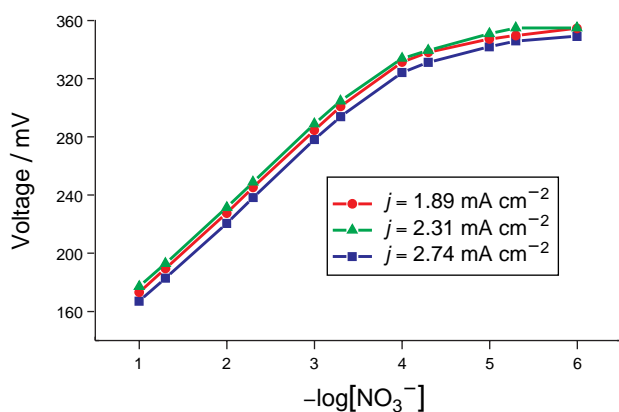


Figure 2. Potentiometric response of polypyrrole electrodes doped with nitrate to NO_3^- ion. Deposition: constant currents of $450 \mu\text{A}$ (circle), $550 \mu\text{A}$ (triangle) and $650 \mu\text{A}$ (square) were applied during 20 min. Electropolymerization solution: 1 M Pyrrole + 0.1 M NaNO_3 . Measurements: 2 days after deposition. Graphite pencil leads: 0.5-mm diameter, 1.5-cm length, $S = 0.24 \text{ cm}^2$.

Table 1. Slopes and Standard Deviation (SD) Calculated for 12 Polypyrrole Electrodes Doped with Nitrate

Electrode	Slope of Electrode Response Curve/mV		
	Current Density 1.89 mA cm^{-2}	Current Density 2.31 mA cm^{-2}	Current Density 2.74 mA cm^{-2}
1	52.4	54.9	54.1
2	54.0	55.1	53.9
3	54.0	55.6	54.6
4	55.5	55.7	55.9
Average \pm SD	54.0 ± 1.3	55.3 ± 0.4	54.6 ± 0.9

Results and Discussion

Nitrate-doped polypyrrole electrodes were tested potentiometrically for their response to NO_3^- two days after deposition. Typical calibration curves obtained for three electrodes deposited at different current densities (1.89 – 2.74 mA cm^{-2}) are shown in Figure 2. Individual and averaged slopes and standard deviation (SD) values for 12 different electrodes plated at three different current densities (four at each current density) and conditions described in Figure 2 are summarized in Table 1.

All electrodes exhibited Nernstian behavior (slopes of 54 – 55 mV per log cycle of nitrate concentration at $T = 22 \text{ }^\circ\text{C}$) with a linear response to nitrate concentrations spanning three orders of magnitude, (0.1 – $1 \times 10^{-4} \text{ M}$ or 6200 – 6.2 ppm of NO_3^-), and a detection limit of $(5 \pm 1) \times 10^{-5} \text{ M}$ (3.7 – 2.5 ppm) of nitrate. This detection limit is significantly lower than safe levels of nitrate in drinking water as regulated by the U.S. Environmental Protection Agency (44 ppm) (18) and the European Community Nitrate Directive (50 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 samples

from environments suspected of being affected by nitrates, such as well water or streams in agricultural regions.

Conclusion

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

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Supplemental Material

Instructions for student, notes for the instructor, and additional experiments are available in this issue of *JCE Online*.

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