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Title

Scaleable nitrate sensors for soil and water observation applications (SEN 6)

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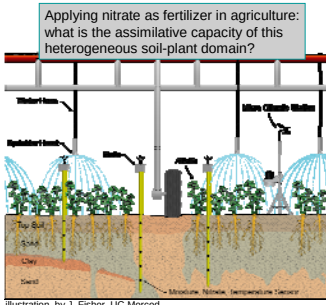
2006

Scaleable Potentiometric Nitrate Sensors for Soil and Aquatic Observation Applications

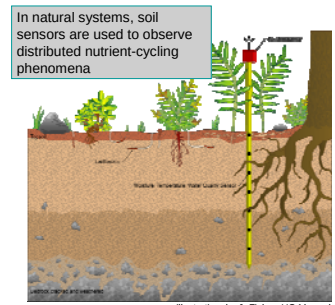
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Introduction: Sensor fabrication in an environmentally relevant form factor



Abstract. Many environmental, agricultural, and ecological water quality problems would be better understood and effectively managed if they could be efficiently and economically observed over time in a spatially distributed manner. Unfortunately, the current selection of commercially available chemical sensors is limited, and those that are available are relatively expensive (\$200 to \$500 ea.), and are generally not optimally packaged for field deployments. Over the past four years, the CENS Sensor group has directed substantial efforts at creating sensitive, selective nitrate sensors with modest power requirements and that are amenable to micro-fabrication methods which will allow the production of large numbers of small sensors. This poster highlights the results of these efforts with respect to **potentiometric mono- and bi-layer nitrate microsensors**. Prototypes of both types of sensors have been successfully tested in the laboratory. Mono-layer nitrate sensors were preliminary tested using real environmental samples and also used for field deployments. *The potentiometric version appears to be less sensitive than the amperometric one, but the potentiometric sensors are easier to fabricate and have been tested in situ in both soil and river systems.*

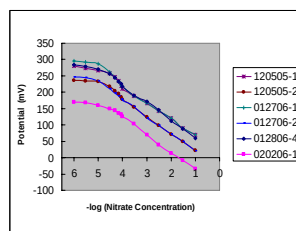
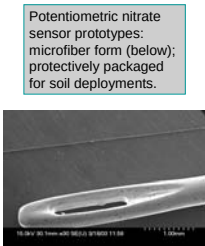


Proposed Solution: Potentiometric Nitrate Microsensors

Approach:

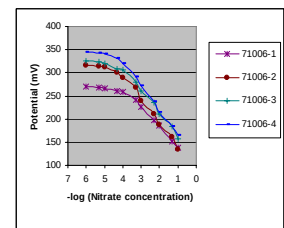
- We are creating **scaleable** nitrate microsensors suitable for dense, spatially distributed deployment in environmental media.
- In addition to precise and accurate, our sensors must be **inexpensive** and have **low impact** on the observations (e.g., avoid flow disturbances)
- We have become adept at fabricating nitrate-doped **potentiometric** ion selective electrodes (ISEs)

Conducting polymer-based nitrate ISEs



Bi-layer nitrate microsensors

- 1st layer - PPy(NO₃) (nitrate doped polypyrrole)
- 2nd layer - Bis-EDOT (bis-ethylenedioxythiophene)
- Show near-Nernstian response (51-53 mV dec of conc), wide linear response range (5.0-6200 ppm), good value of detection limit (1-4 ppm)



- Mono-layer sensor performance (competitive with commercial nitrate sensors)
 - Broad linear response range Detection limit as low as 30-80 uM (2-5 ppm)
 - Highly selective over other ions (see below)
- Limitation: short-lived under flow-through conditions (but reconditionable!)

Calibration curves of **mono-layer** (PPy(NO₃)) electrodes; legend indicates fabrication date (MM/DD/YY).

Calibration curves of **bi-layer** (PPy(NO₃)+Bis-EDOT) electrodes (all 4 sensors were prepared using different polymerization times for 1st layer (PPy(NO₃)) – 5,10,15,20 min for sensors 71006-1, 1,2,3,4 correspondingly). Legend indicates sensor fabrication date (MM/DD/YY).

Results: Prototype testing in the lab; scale-up to CENS test beds

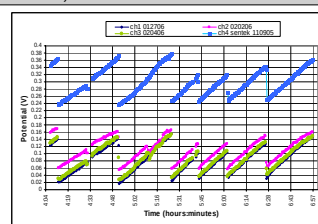
Testing microsensor utility: direct soil and water nitrate probing

- The potentiometric sensors have been tested for conditions ranging from the beaker to the field
- Results below are for:
 - Selectivity testing
 - Flow-through water and soil tests
 - In situ soil testing



Prototype testing

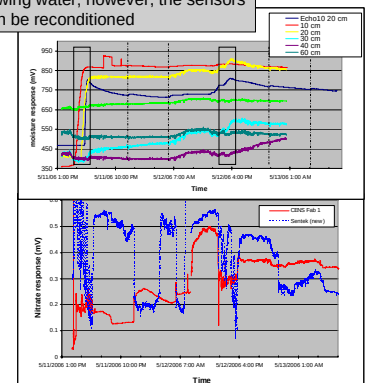
Deionized water test-bed experiment (continuous water flow). Mono-layer (PPy(NO₃)) sensors (legend indicates sensor fabrication date) and Nitrate ISE (Sentek Ltd)



Deployment at Palmdale test bed



3-day deployment at Palmdale: PPy(NO₃) sensors loose their sensitivity during direct exposure to flowing water; however, the sensors can be reconditioned



Selectivity

Potentiometric selectivity coefficients for PPy(NO₃) electrodes

J ⁻ (interfering anion)	PPy(NO ₃) pencil lead-based ISE (K ^{pot} values)
HCO ₃ ⁻	3.8 x 10 ⁻³
Cl ⁻	1.20 x 10 ⁻²
PO ₄ ³⁻	2.00 x 10 ⁻⁴
Br ⁻	9.10 x 10 ⁻²
NO ₂ ⁻	2.22 x 10 ⁻⁴
ClO ₄ ⁻	2.93 x 10 ⁻³

Flow through experiment comparing fabricated sensors with Sentek commercial sensor in soil box.

Future directions

Development of sensors suitable for long-term deployment will require:

- Incorporate **conductive polymers** with longer life cycles (possible solution – bi-layer electrodes – additional field tests will be performed)
- Incorporate materials **resisting biofouling** and/or development of systems for **sample pretreatment** (e.g., automated microfluidic prefiltration)
- Develop different types of sensor packaging for direct nitrate measurement in soil and local rivers