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Micro- and Mini-nitrate Sensors for Monitoring of Soils, Groundwater and Aquatic Systems

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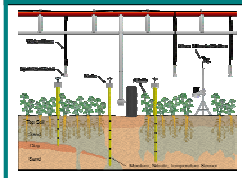
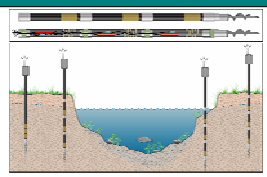
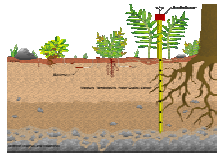
Introduction: Needs for scaleable nitrate sensing in environmental assessment



Applying nitrate as fertilizer in agriculture: what is the assimilative capacity of this heterogeneous soil-plant domain?



Describing transport of chemical substances within river systems: estimation of mass transfer across the rivers surface water – groundwater interface using javelin platforms



In natural systems, soil sensors are used to observe distributed nutrient-cycling phenomena

Abstract Inorganic nitrogen (nitrate, NO3-) is a major source of pollution in groundwater, surface water and the air. Application of nitrate-containing fertilizers can create distributed or non-point source pollution problems. Scalable nitrate sensors (sensors which are small and inexpensive) would enable us to better assess non-point-source pollution processes in agronomic soils, groundwater and rivers. Sensor research groups in the CENS have been working toward high-performance scalable nitrate sensors using *potentiometric*, *amperometric*, and *spectrochemical* methods. (1) Ion-selective electrode (potentiometric sensor) is the simplest in terms of instrumentation and fabrication, and showed an excellent dynamic range and good sensitivity. The sensor has been tested in the field and various polymer coatings are applied to improve reliability in soil. (2) The more complex amperometric sensor is fabricated using micromachining, and tested in the lab. The sensor presented a large dynamic range and excellent sensitivity. The novel sample preparation system using anion-exchange membrane is also designed to improve selectivity. This research is completed. (3) New addition to the nitrate sensor research is a micro optical sensor, based on UV absorption. Optical sensing shows superior reliability and sensitivity to electrochemical methods. Currently, the analytical technique is studied in macro-scale using a bench-top

Proposed Solution: Nitrate micro- and mini-sensors

Potentiometric Nitrate Mini-Sensor with PVC membrane containing liquid anion-exchanger

Slope of electrode function	(-53) – (-57) mV/decade
Linear range	10^{-5} – 10^{-1} M (0.62-6200 ppm)
Lower detection limit	0.062-0.186 ppm NO_3^-
Operating pH range	2 - 8.5
Main interfering anions*	Cl^-, Br^-

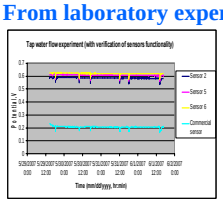
*H.J.Kim, J.W. Hummel, S.J. Birrell, Trans of the ASABE, 2006, vol. 49 (3), p. 597

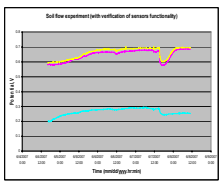
Commercial sensor

Mini-sensor

Circuit boards have been designed to make mini-sensors *compatible* with commercial data logger

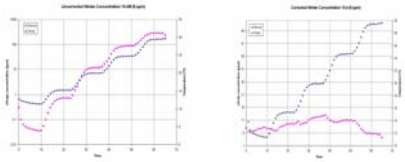
From laboratory experiments …





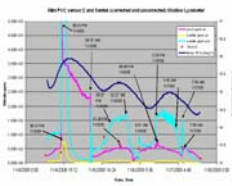
Mini-sensors with PVC maintain their sensitivity during 3 days exposure to tap water flow

Soil test-bed: CENS-*fabricated* mini-sensors with PVC membranes showed **better** response in soil than *commercial* one



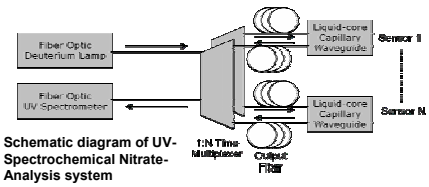
Commercial nitrate sensor at constant concentration with variable temperature prior to (left) and after (right) application of temperature correction algorithm

to the field...

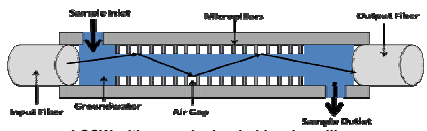


- Observing cyclical nitrate readings (beyond T effects) under field conditions (irrigation with manure water)
- Challenge to reproduce using traditional sampling techniques

Micromachined Spectrochemical Nitrate Sensor



Schematic diagram of UV-Spectrochemical Nitrate-Analysis system



LCCW with super-hydrophobic micropillars

- **Absorption spectrophotometry in UV region**
- **Liquid-core capillary waveguide (LCCW) for miniaturized and sensitive optical sensing**
- **Superior long-term reliability**
- **Multiplexible: fiber optics, miniature spectrometer, and UV source:.**

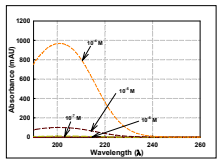
MVA (Multivariate Analysis)

- **Nitrate is measured with absorbance spectra using a modified Beer's law :**

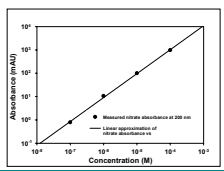
$$A_\lambda = b \cdot \left(\sum_J \varepsilon_{\lambda,J} \cdot C_J + e + f \cdot \lambda + g \cdot \lambda^2 \right)$$

λ : **wavelength,** C_J**: concentration of Jth chemical species,** b : **the optical path length,** A_λ**: the absorbance at wavelength,** $\varepsilon_{\lambda,J}$**: the molar absorptivity,** e**,** f**, and** g**: background coefficients**

- **Least-mean-square method to approximate the concentration of multiple chemical species and reject background signal**
- **Linear calibration from 10^{-7} to 10^{-4} M**

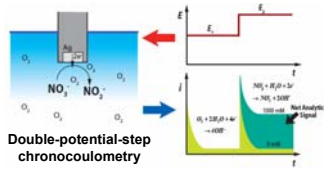


Nitrate absorption spectra measured with Lambda 20 spectrophotometer at four different concentrations.

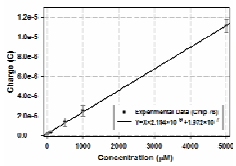


Calibration curve at λ = 200 nm

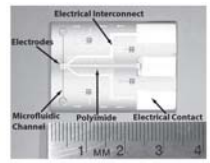
Micromachined Amperometric Nitrate Sensor



Double-potential-step chronocoulometry



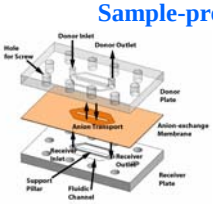
Calibration curve



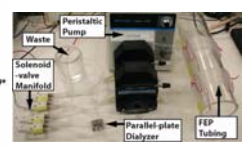
Microfabricated Sensor Chip

- **Double-potential-step chronocoulometry of nitrate: improved SNR, no oxygen interference**
- **Silver working electrode in 0.01 M NaOH**
- **Microfabricated electrodes and microfluidic channels on a silicon substrate (small form factor)**
- **Low detection limit (4-75 μM), and large dynamic range (2-4 orders)**
- **Interference : PO_4^{3-}, Ca^{2+}, and Sr^{2+}**

Sample-preparation System



Parallel-plate Dialyzer



Experimental Setup

- **Donnan-dialysis-based ionic filtration system**
- **Anion-exchange membrane (cation/large neutral species/slow anions removed)**
- **Parallel-plate and microfluidic channels (microfabricable)**
- **Small solution volume (<10 ml), linearity, high sample throughput**
- **FDM-based numerical analysis to predict dialysis performance**
- **Throughput: 1 sample/hr**

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UCLA – UCR – Caltech – USC – CSU – JPL – UC Merced

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