Title
A High-Performance Micromachined Amperometric Nitrate Sensor for Environmental Monitoring (SEN 8)

Authors
Dohyun Kim
Ira B. Goldberg
Michael Glickman
et al.

Publication Date
2006

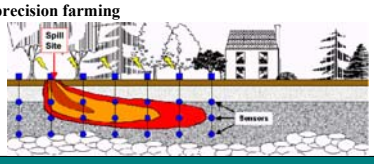
A High-Performance Micromachined Amperometric Nitrate Sensor for Environmental Monitoring

Dohyun Kim, Ira B. Goldberg, Michael J. Glickman and Jack W. Judy
UCLA Electrical Engineering Department – www.ee.ucla.edu/research/judylab

Introduction: Why a Micromachined Amperometric Nitrate Sensor?

Why Nitrate (NO_3^-) Sensor Important?

- Nitrate is a major contaminant in ground water
- Nitrate-sensor applications
  - *In situ* nitrate monitoring, environmental science/engineering research, and precision farming



Electrochemical Methods

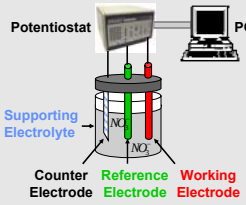
- Nitrate-sensor requirements
  - Inexpensive, small, remotely operable, and large detection range (0.1 μM to 1 mM)
- Electrochemical techniques meet the requirements
  - Simple design and operation
  - Easy miniaturization
  - Low power consumption
  - Good sensitivity

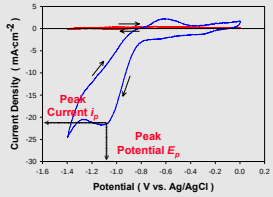
Glucose Sensor

Ion-Selective Electrode

Working Principle: Amperometric Detection of Nitrate and Anion Permeable Membrane

Electrochemical Study





- The highest sensitivity was achieved with an electrochemical system (NaOH electrolyte, Ag working , Ag/AgCl reference, Pt counter electrode. $NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$

Removing Oxygen Interference

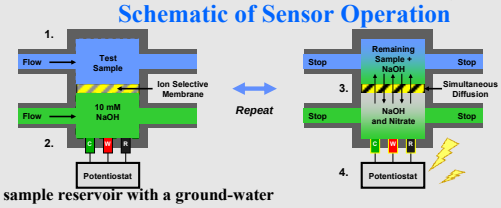
- Oxygen in electrolyte (≅ 0.26 mM) increases background signal
- Nitrate reduction current = (nitrate + oxygen reduction current) – (oxygen reduction current)

Anion Permeable Membrane

- Many ionic/non-ionic species that interferes with nitrate measurement in groundwater
- Reduce interference with an anion-permeable membrane
  - No cation transport
  - Faster nitrate transport than the other anions

Tokuyama ACS Membrane

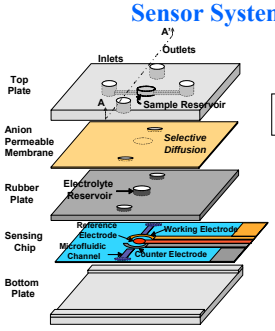
Schematic of Sensor Operation

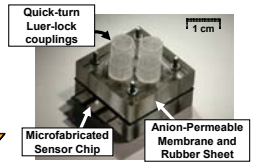


1. Fill sample reservoir with a ground-water
2. Fill microelectrochemical (MEC) cell with electrolytic eluent (10 mM NaOH)
3. OH^- and NO_3^- diffuse across anion-permeable membrane in opposite directions
4. Perform measurements when concentrations reach equilibrium

Design, Fabrication, Experimental Results, and Summary

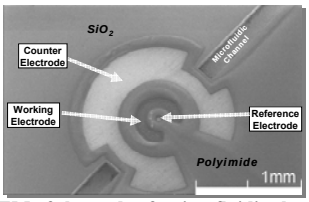
Sensor System Integration





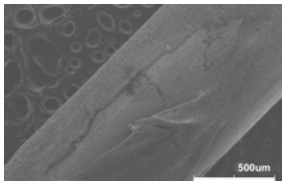
Assembled Sensor Unit

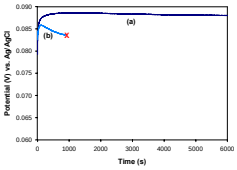
Micromachined Nitrate Sensing Chip



SEM of electrodes & microfluidic channel

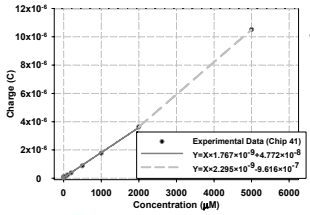
- Pt counter electrode (7.7× 10^{-3} cm^2)
- Ag working electrode (0.7×10^{-3} cm^2)
- Silver oxide reference electrode (0.038×10^{-3} cm^2)
- polyimide insulation layer





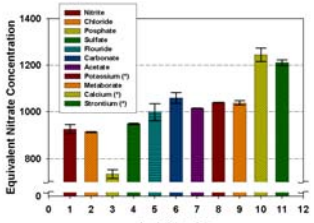
SEM of *polyurethane*-coated Ag/AgCl reference electrode and its potential drift (a) in comparison to silver oxide electrode (b). The minimal potential drift observed (3 mV for 27 hours)

Experimental Result



- Sensor performance
  - Linear up to 500~2000 μM
  - Detection limit: 4~75 μM
  - r^2=0.99 linearity

Calibration Curves of a Micromachined Sensing Chip for Nitrate Standards (0 ~ 5000 μM)



Measured nitrate concentration when 1000 μM of interfering ionic species are added to 1000 μM nitrate.

- There was no significant interference from other ionic species when nitrate is not present
- PO_4^{3-}, Ca^{2+}, and Sr^{2+} shows significant interference when nitrate present

- Anion permeable membrane and selectivity to interfering ions
  - Sensor output to a mixture of 100 μM nitrate and interfering ions (100 μM each of PO_4^{2-}, SO_4^{3-}, F^-, Cl^-) is only 13.9% higher than the average response for the sample consisting of only nitrate

Future Work

- Field test (Palmdale site, Merced river in NIMS platform, etc.)
- Fluidic components and μ-potentiostat integration (in conjunction with *Sample Preparation Project*)
- Integrate into wireless motes and remote measurement test
- Integration of PU-coated Ag/AgCl reference electrode