Title

SEN1: A High-Performance Micromachined Amperometric Nitrate Sensor for Environmental Monitoring

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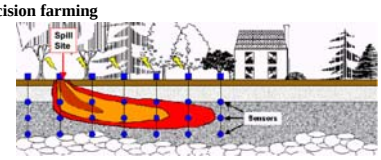
Introduction: Why a Micromachined Amperometric Nitrate Sensor?

Why Nitrate (NO_3^-) Sensor Important?

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



- Sensor requirements
  - Inexpensive, small, remotely operable, detection range (1 µM to 1 mM)

Current Analytical Methods vs. Electrochemical Methods

Ion Chromatography

Spectrochemical and Separation Method:
- Spectroscopy, Chromatography, Electrophoresis, etc.
- Large/expensive equipment
- Relatively complex operation and sample preparation
- High voltage, pressure, and power

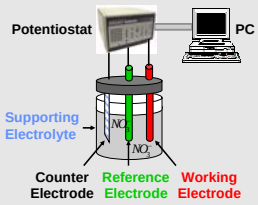
Electrochemical Method:
- Amperometry and Potentiometry
- Simple design and operation
- Easily minaturized
- Low power & voltage
- Sensitive

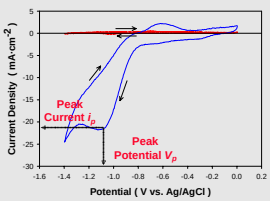
Glucose Sensor

Ion-Selective Electrode

Working Principle: Electroanalytic Chemistry and Anion Permeable Membrane

Electrochemical Study





- Electrochemical reduction of nitrate: $NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$
- NaOH supporting electrolyte, working electrode (Ag), reference electrode (Ag/AgCl), counter electrode (Pt)

Removing Oxygen Interference

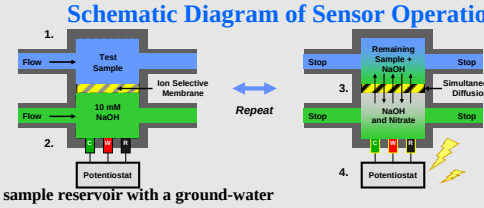
- Oxygen in electrolyte (≅ 0.26 mM) interferes with detection
- Nitrate reduction current = (nitrate + oxygen reduction current) – (oxygen reduction current)

Anion Permeable Membrane

- Ground water contains many ionic/non-ionic species interfering nitrate measurement
- Selective measurement with an anion selective membrane
  - Anion-permeable membrane blocks all cations
  - Nitrate diffuse faster than the other interfering ions

TokuyamaACS Membrane

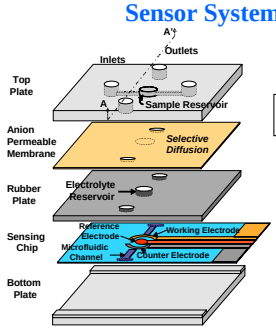
Schematic Diagram of Sensor Operation

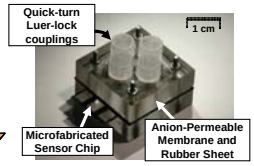


1. Fill sample reservoir with a ground-water
2. Fill microelectrochemical (MEC) cell with electrolytic eluent (10 mM NaOH)
3. OH^- and NO_3^- diffuse across anion-permeable membrane in opposite directions
4. Perform measurements when concentrations reach equilibrium

Design, Fabrication, Experimental Results, and Summary

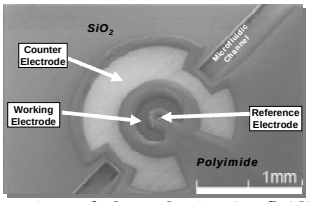
Sensor System Integration





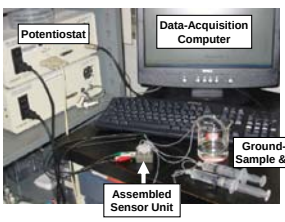
Assembled Sensor Unit

Electrodes, Microfluidic Channels, and Experimental Setup



SEM of Electrodes & Microfluidic Channel

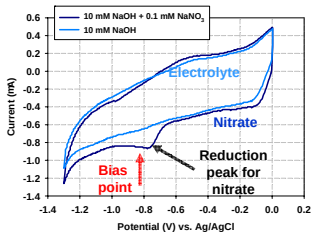
- Pt counter electrode (7.7x 10^{-3} cm^2)
- Ag working electrode (0.7×10^{-3} cm^2)
- Silver oxide reference electrode (0.038×10^{-3} cm^2)
- polyimide insulation layer

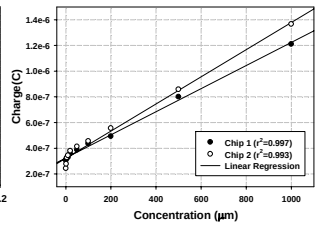


- Electrochemical detection by computer-controlled potentiostat
- Eluents and ground-water sample are injected with syringes

Bench-top Experimental Setup

Experiment: Calibration Curves and Sensor Selectivity





- Calibration curves (1 to 1000 µM)
  - Working electrode biased at -0.9 V vs. Ag/AgCl
  - Integrated nitrate reduction current for 0.5 sec
- Detection limit: ~1 µM
- Nitrate sensor selectivity
  - Measure sensor response to a mixture of 100-µM nitrate and typical interfering ions (100 µM each of PO_4^{2-}, SO_4^{3-}, F^-, Cl^-)
  - The sensor output increases only 13.9% higher than the average response for the sample consisting of 100-µM nitrate

Summary and Future Work

- Sensitive amperometric nitrate sensors are feasible with
  - Ag working electrode and NaOH supporting electrolyte
- Prototype nitrate sensor units have been fabricated and tested
  - Microelectrodes and integrated microchannels
  - Anion-permeable membrane (acceptable selectivity)
  - Achieves a detection limit of ~1 µM
- Future work
  - Thick working electrode (thin film Ag has a limitied life time)
  - Better reference electrode (Ag/AgCl with polymer coating being studied)
  - Long-term qualification tests and field test
  - Integrate into wireless sensor motes and network