Title
Micromachined Amperometric Nitrate Sensor

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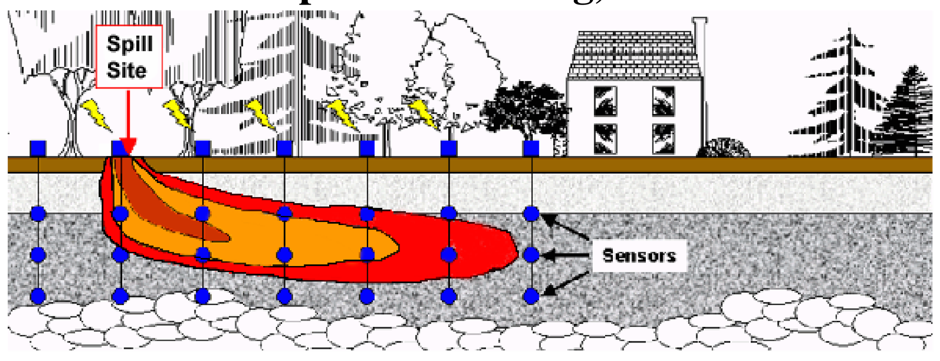
Introduction : Why an Amperometric Nitrate Sensor?

Why Nitrate (NO_3^-) Sensor Important?

- Nitrate is a major contaminant in ground water system
- Nitrate-sensor applications
  - In-situ nitrate monitoring
  - Environmental science and engineering (contaminant transport monitoring, contaminant source assessment)



- Sensor requirements: inexpensive, small, remotely operable, low detection limit (1 μM to 1 mM)

Current Analytical Methods vs. Electrochemical Methods


Ion Chromatography

Current Analytical Methods:
Spectroscopy, Chromatography, Electrophoresis…
- Large/expensive equipment
- Relatively complex operation and sample preparation
- Currently use relatively high voltage, pressure, or power

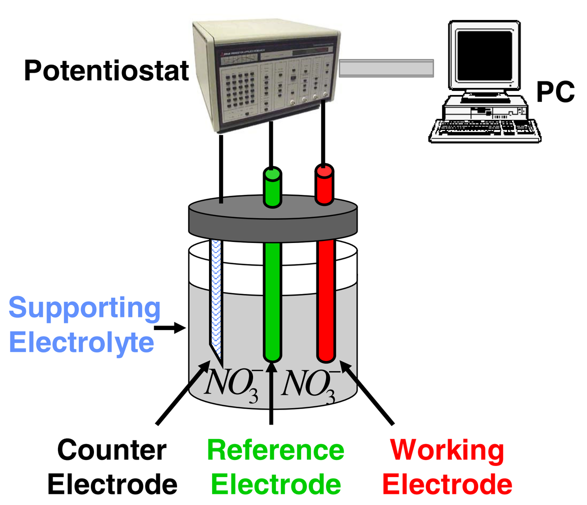
Electrochemical Method:
- Amperometry or Potentiometry
- Simple design and operation
- Easily minaturized
- Low power & voltage
- Sensitive techniques

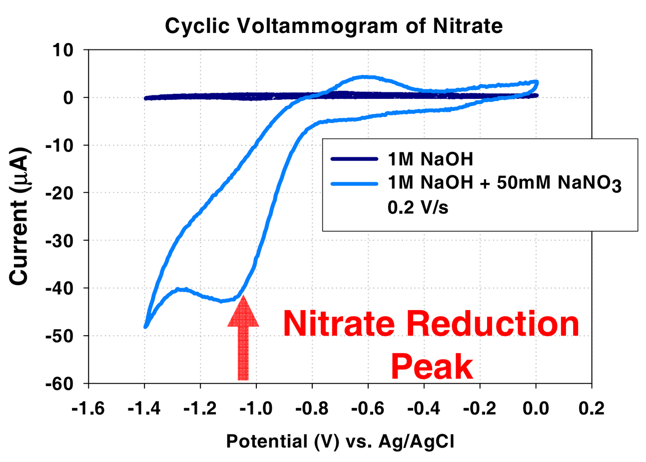

Glucose Sensor


Ion-Selective Electrode

Working Principle : Electrochemistry and Anion Permeable Membrane

Electrochemical Study for Amperometry of Nitrate





- 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

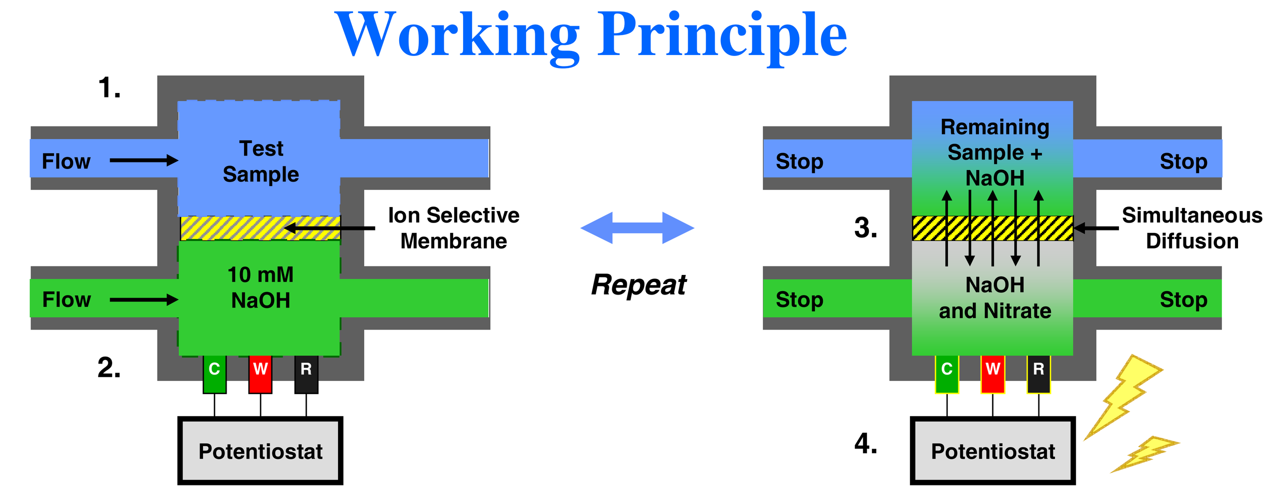
- Oxygen dissolved in ground water (≅ 0.26 mM) interferes with the nitrate detection
- A simple and effective differential approach :
  Nitrate reduction current = (nitrate + oxygen reduction current) – (oxygen reduction current)

Anion Permeable Membrane

- Selectivity is a critical chemical sensor issue
- Ground water contains many ionic species: (e.g. Ca^{2+}, Mg^{2+} , Cl^-, HCO_3^-, SO_4^{2-}, H_2CO_3, B, NO_3^-, CO_3^{2-}, K^+, Fe^{3+} , F^- , PO_4^{3-}, HPO_4^{2-}, trace metals)
- Nitrate-selective membrane (Tokuyama ACS)
  - Anion-permeable membrane blocks all cations
  - Nitrate diffuse faster than the interfering ions


Anion-Permeable Membrane

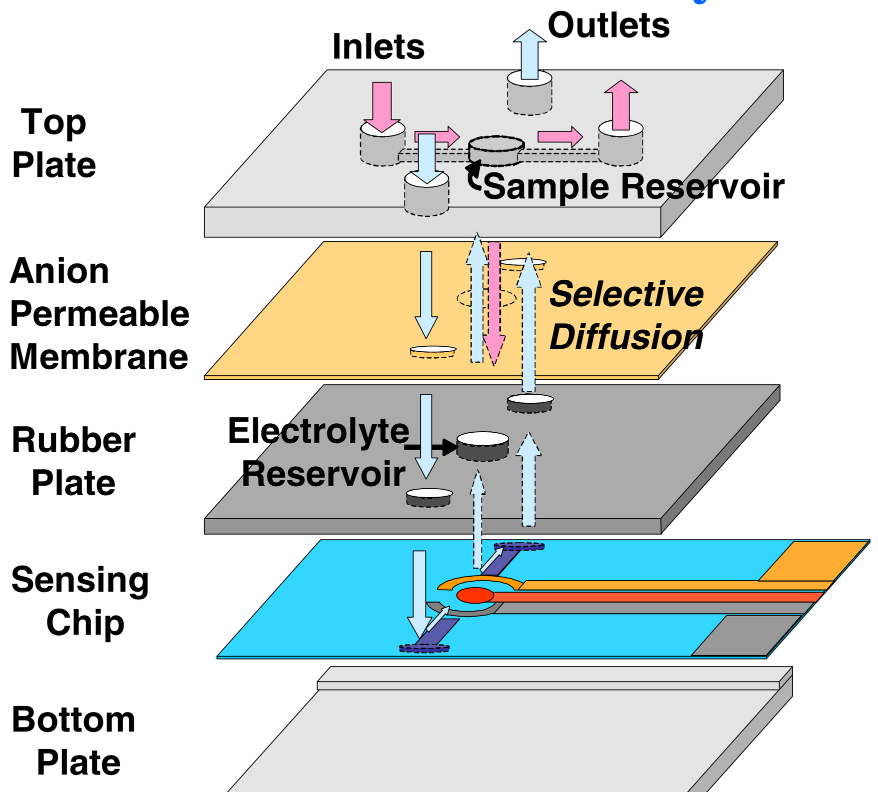
Working Principle

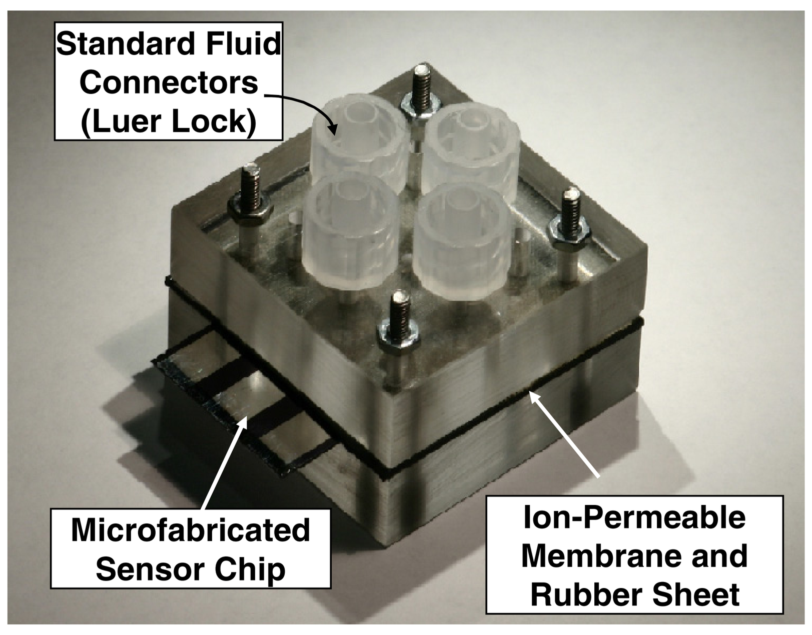


1. The sample reservoir is filled with a ground-water
2. The microelectrochemical (MEC) cell is filled with an electrolytic eluent (10 mM NaOH)
3. Hydroxide and nitrate ions diffuse across anion-permeable membrane simultaneously
4. Electrochemical measurements are performed after reaching equilibrium

Design, Fabrication, and Experimental Results

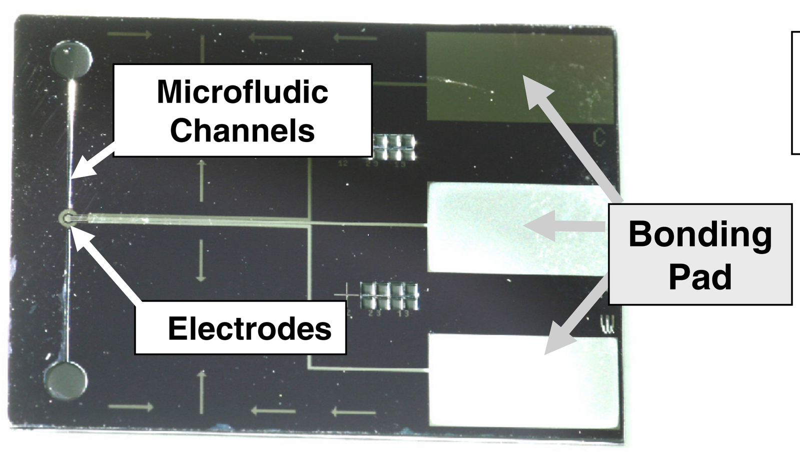
Sensor System Integration



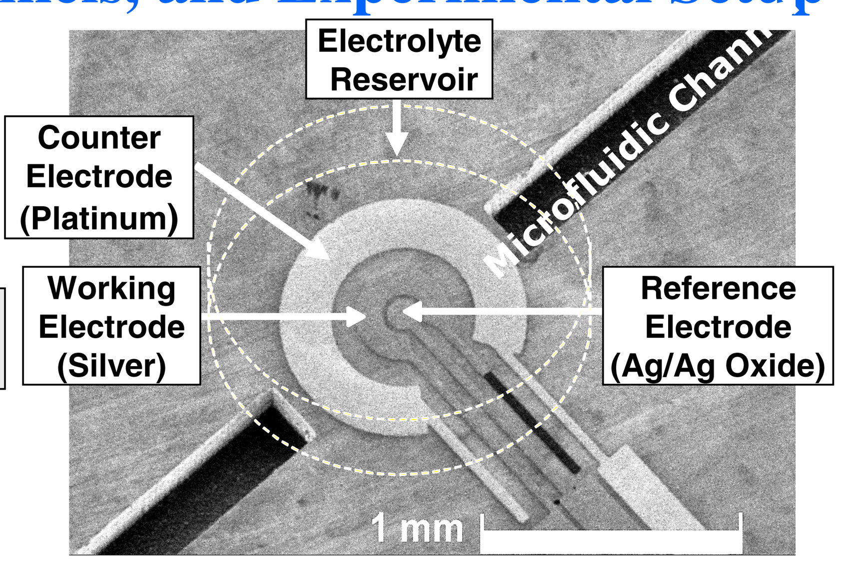


- Reservoir volume: 1.8 μL
- Diffusion time: ~5 min

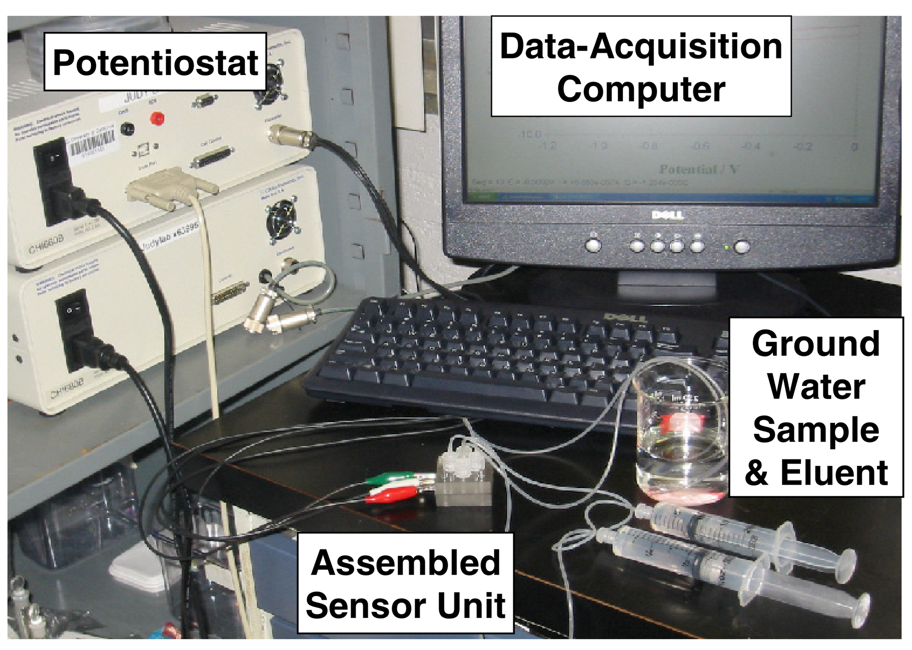
Electrodes, Microfluidic Channels, and Experimental Setup



Microfabricated Sensor Chip



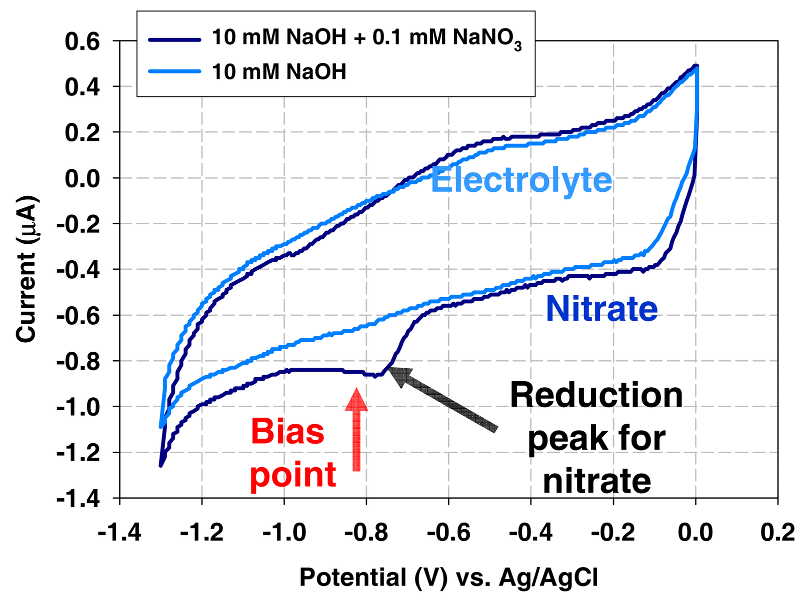
SEM of Electrodes & Microfluidic Channel

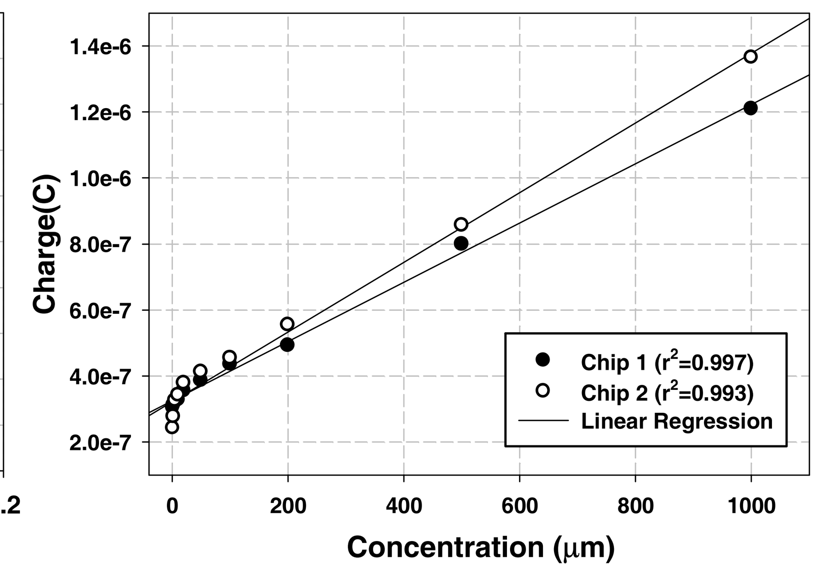


- Electrochemical detection by computer-controlled potentiostat
- Eluents and ground-water sample are injected with syringes

Bench-top Experiemental Setup

Experiment: Calibration Curves and Sensor Selectivity





- Calibration curves
  - Working electrode biased at -0.9 V vs. Ag/AgCl
  - Integrated nitrate reduction current for 0.5 sec
- Detection limit is ~1 μM
- Nitrate sensor selectivity
  - Measure sensor response to a 100-μM-nitrate sample
  - 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

Conclusion

- Sensitive amperometric nitrate sensors are feasible with
  - Silver working electrode
  - NaOH supporting electrolyte
- Selective prototype sensor units have been designed, fabricated, assembled, and tested
  - Chip with microelectrodes and integrated microchannels
  - An anion-permeable membrane (acceptable selectivity)
  - Achieves a detection limit of ~1 μM
- Future work
  - Long-term qualification tests
  - Field tests
  - Integrate into wireless sensor motes and network