Why Nitrate (NO₃⁻) 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

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

Electrochemical Study for Amperometry of Nitrate

- Electrochemical Reduction of Nitrate: \( \text{NO}_3^- + H_2O + 2e^- \rightarrow \text{NO}_2^- + 2OH^- \)
- 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) – nitrate detection

Anion Permeable Membrane

- Selectivity is a critical chemical sensor issue
- Ground water contains many ionic species: (e.g. Ca²⁺, Mg²⁺, Cl⁻, HCO₃⁻, SO₄²⁻, H₂CO₃, B, NO₂⁻, CO₃²⁻, K⁺, Fe³⁺, F⁻, PO₄³⁻, HPO₄²⁻, trace metals)
- Nitrate-selective membrane (Tokuyama ACS)
  - Anion-permeable membrane blocks all cations
  - Nitrate diffuse faster than the interfering ions

Working Principle: Electrochemistry and Anion Permeable Membrane

Design, Fabrication, and Experimental Results

- Design, fabrication, and experimental results
- Electrodes, Microfluidic channels, and experimental setup
- Sensor system integration
- Bench-top experimental 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 PO₄³⁻, SO₄²⁻, 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