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A High-Performance Micromachined Amperometric Nitrate Sensor for Environmental Monitoring

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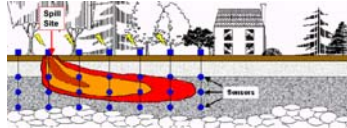
Introduction: Why a Micromachined Amperometric Nitrate Sensor?

Why Nitrate (NO₃⁻) Sensor Important?

- Nitrate is a major contaminant in ground water: cause human health risks (e.g. *methemoglobinemia*)
- Nitrate-sensor applications: *In situ* nitrate monitoring, environmental science/engineering research, and precision farming



Infants *methemoglobinemia*



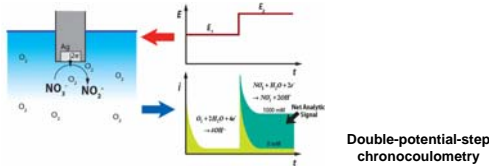
Distributed sensors for contaminant-source assessment

Electrochemical Methods

- Nitrate-sensor requirements
 - Inexpensive, small, remotely operable, and large detection range (0.1 μM to 1 mM)
- Electrochemical techniques meet the requirements
 - High sensitivity (0.1 ~ 1 μM) and good dynamic range (1-10 mM)
 - Relatively simple operation
 - Easy miniaturization
 - Low power consumption

Working Principle: Amperometric Detection of Nitrate

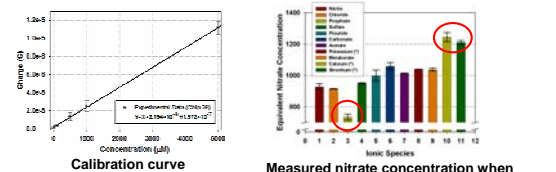
Amperometric Detection



Double-potential-step chronocoulometry

- Electrochemical reaction on the sensing electrode and measured current is dependent to nitrate concentration
 $NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$
- Proposed electrochemical system: NaOH electrolyte, Ag working, Ag/AgCl reference, and Pt counter electrode.
- Double-step chronocoulometry: less noise and minimize O₂ interference

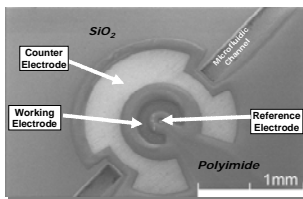
Nitrate Analysis



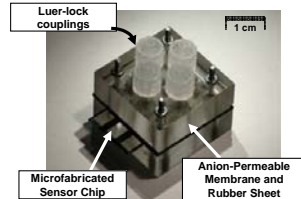
- High sensitivity: 2.47 A·s^{1/2} / (V^{1/2}·M·cm²) – better than other electrochemical system
- Low detection limit: ~4 μM
- Wide dynamic range : ~4 to 10000 μM
- Interference : PO₄³⁻, Ca²⁺, and Sr²⁺ shows significant interference (20% signal distortion)

Micromachined Nitrate Sensor: Design, Fabrication, Experimental Results, and Summary

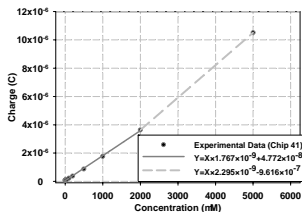
Micromachined Nitrate Sensor



SEM of electrodes & microfluidic channel



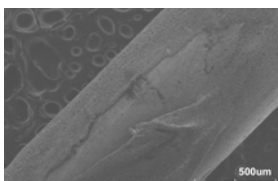
Assembled sensor unit



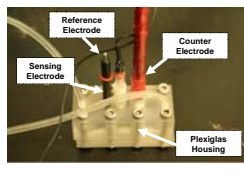
- Sensor performance
 - Linear up to 500~2000 μM
 - Detection limit: 4~75 μM
 - r²=0.99 linearity

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

Improvement in Sensor Reliability



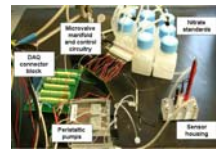
SEM of polyurethane-coated Ag/AgCl reference electrode



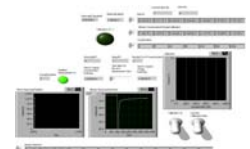
Sensor housing with commercial electrodes

- PU-coated electrode is more stable (3 mV drift/day)
- Macro-sized Ag sensing electrode and Ag/AgCl reference electrode: virtually infinite life-time

Toward Field-deployable Stand-alone Nitrate Sensor

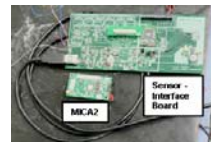


Experimental setup for automatic nitrate sensing system

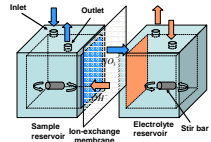


LABVIEW control panel for auto-calibration and sensing

- LABVIEW-based automatic nitrate sensing and calibration
 - LABVIEW control valves manifold, potentiostat and peristaltic pumps
 - Automatic sensor calibration from 0 to 1000 μM
 - Uninterrupted continuous sensing (adjustable time interval)



Sensor-interface board and MICA2 daughter board



Sample processor

- Palm-sized sensor-interface board with microprocessor, wireless capability, and built-in potentiostat is being developed
 - 8 bit microcontroller, SOS operating system, valve and pump control circuitry
 - Can replace bulky, expensive, power-hungry potentiostat
 - MICA 2 daughter board for wireless telemetry
- Donnan-dialysis-based sample processor (filtration unit)
 - Nitrate-specific anion-exchange membrane would improve selectivity to groundwater that contains many ionic species
 - Numerical simulation and experimental analysis making progress

Future Work

- Groundwater testing and comparison with conventional bench-top analysis techniques
- Field test (Palmdale site, Merced river etc.)