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MICROMACHINED AMPEROMETRIC NITRATE SENSOR WITH AN ANION PERMEABLE MEMBRANE

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ABSTRACT

A nitrate-sensing system that consists of a micromachined sensor substrate, anion-permeable membrane, integrated microfluidic channels, and standard fluidic connectors has been designed, fabricated, assembled, and tested. Our microsensor was designed for *in-situ* monitoring of nitrate concentrations in ground water. A silver electrode was patterned for amperometric nitrate detection. An electrochemically oxidized silver electrode was used as a reference electrode. Microfluidic channels were fabricated as flow paths to the microelectrochemical (MEC) cell for the eluent and ground-water sample. The sensor also incorporates an anion-permeable membrane that is used for selective measurement of nitrate. With standard addition methods, linear calibration curves have been obtained and the detection limit is ~1 μM. To test selectivity, the sensor response to a 100-μM-nitrate solution and a mixture of nitrate and interfering ions (100 μM each of NO_3^-, PO_4^{-2}, SO_4^{-3}, F^-, and Cl^-) were compared. Despite the 400% increase in total ionic concentration, the sensor output only increased 13.9%.

I. INTRODUCTION

Nitrate is considered to be a major contaminant in ground-water and surface-water systems, and can present significant risks to human health and the environment [1]. In addition, precise nitrate-concentration management is needed for the growing field of precision farming [2]. Consequentially, federal health and environmental agencies, ecological scientists, environmental engineers, and farmers have a great need for small, low-power, reliable, and yet sensitive nitrate sensors that can be remotely operated and can measure concentrations in the range of 1 μM to 1 mM [3].

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Commercially available nitrate-sensing systems based on ion chromatography, spectrometry, or electrophoresis, usually require expensive and massive instrumentation, complex measurement procedures, and are not currently amenable to remote operation or large-scale deployment. Electrochemical measurements, such as amperometry and potentiometry, are relatively simple, easily miniaturizable, low power, and yet sensitive enough for the targeted applications (i.e., 1 μM to 1 mM). Of these electrochemical techniques, amperometry usually offers a higher precision and lower detection limit than potentiometry [4].

Selectivity is a major concern in electrochemical measurements and many surface-modification approaches have been proposed, including immobilized enzymes, freshly-deposited electrode surfaces, and complexing metal ions. However, these approaches increase technical and procedural complexity, without significantly improving performance [4]. Instead, an anion-permeable membrane provides the selectivity for our sensing system.

Our ultimate research goal is to develop a remotely operable, field-deployable, and miniaturized nitrate-sensing system that meets the requirements mentioned above. With sensitive amperometric detection techniques, an anion-permeable membrane, and MEMS-fabrication technology, such a sensing system can be realized.

II. WORKING PRINCIPLE

Nitrate undergoes reduction in alkaline media with relatively small negative polarization potential [5]:

$$\begin{aligned} &NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \qquad E^0 = -0.23\ V \text{ (vs. SCE)} \\ &NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^- \qquad E^0 = -0.41\ V \text{ (vs. SCE)} \end{aligned} \tag{1}$$

Despite the thermodynamic possibility of the above reactions, the reaction kinetics are slow. Consequently, a typical metal electrode such as platinum, gold, and glassy carbon can only obtain a poor sensitivity. Metals in Group Ib (Cu and Ag) and Group IIb (Zn and Cd) shows the high activity in reducing nitrate [6]. Several groups have studied nitrate reduction on silver electrodes and have reported that silver has an excellent activity in reducing nitrate to nitrite or ammonia [7-9]. Electrochemical reduction of nitrate in alkaline media is of interest since interference from hydrogen evolution can be minimized by increasing the hydrogen reduction potential in the negative direction. After thorough cyclic voltammetric studies of nitrate (Figure 1) with a silver disk electrode (Bioanalytical System, Inc.) in NaOH electrolyte, we concluded that silver is sensitive enough for our purpose and that a silver working electrode can be microfabricated for our sensor system.

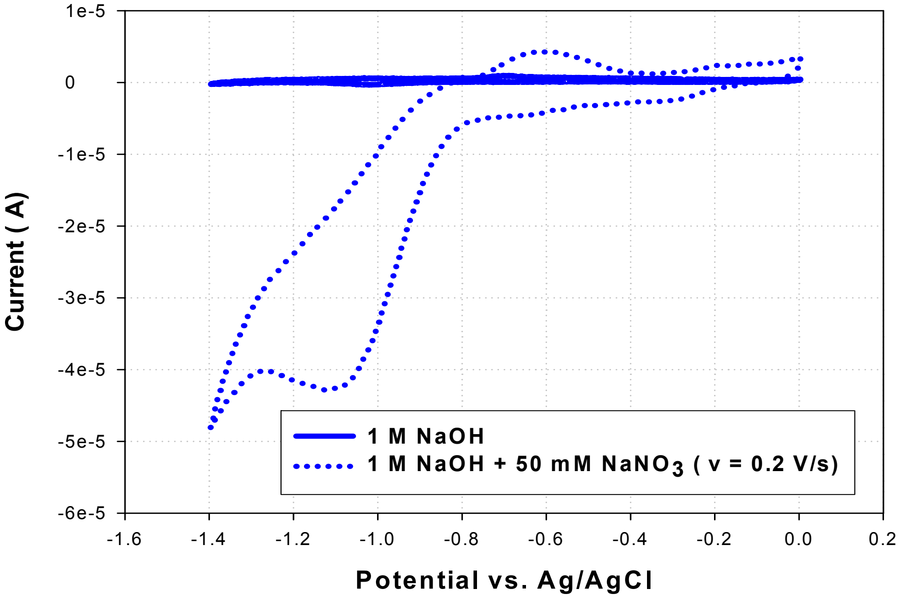

Figure 1. Cyclic voltammery of 50-mM nitrate in 1 M-NaOH electrolyte and only in 1 M NaOH electrolyte.

A schematic diagram of the sensing system and an illustration of its operation are shown in Figure 2. The reservoir for the ground-water sample and the microelectrochemical cell (MEC) are adjacent to each other but separated by the anion-permeable membrane. An inlet and outlet microfluidic channel are connected to each MEC cell and the sample reservoir, in order to supply and remove the solutions (Figure 2a). The sample reservoir is filled with a ground-water test sample and the microelectrochemical (MEC) cell is filled with an electrolytic eluent (10 mM NaOH) (Figure 2b). Hydroxide ions diffuse across the membrane due to an extreme concentration gradient, while nitrate ions diffuse through the membrane and enter the cell to maintain charge balance. After equilibrium is reached, the nitrate ions previously in the sample reservoir are transferred to the MEC cell and the amperometric measurements are performed (Figure 2c). When other anions are present in sample solution, they are also transferred across the membrane. However, nitrate diffuses much faster than the other interfering ions due to its larger diffusion coefficient in the membrane. Such a separation method is called Donnan dialysis and ion transport through a membrane follows the Nernst-Plank equation [5, 6], which is given by

$$\frac{dC_{A,1}}{dt} = -\frac{D_A D_B Q S}{(D_A - D_B) L V_1} \times \ln\left(\frac{\dfrac{(D_A - D_B) C_{A,1}}{C_{T,1}} + D_B}{\dfrac{(D_A - D_B)(M_{A,T} - C_{A,1} V_1)}{C_{T,2} V_2} + D_B} \right), \qquad (2)$$

with $C_{T,1} = C_{A,1} + C_{B,1}$, $C_{T,2} = C_{A,2} + C_{B,2}$, $M_{A,T} = C_{A,1}V_1 + C_{A,2}V_2$, and $M_{B,T} = C_{A,2}V_1 + C_{B,2}V_2$,
diffusion coeficient of species A and B through the membrane D_A and D_B,
volume of ground water V_1, volume of microelectrochemical cell V_2, area of membrane S,
thickness of membrane L, membrane capacity Q,
total molarity of species in ground water $C_{T,1}$, total molarity in the cell $C_{T,2}$,
total molarity of the A species $M_{A,T}$, and total molarity of the B species $M_{B,T}$.

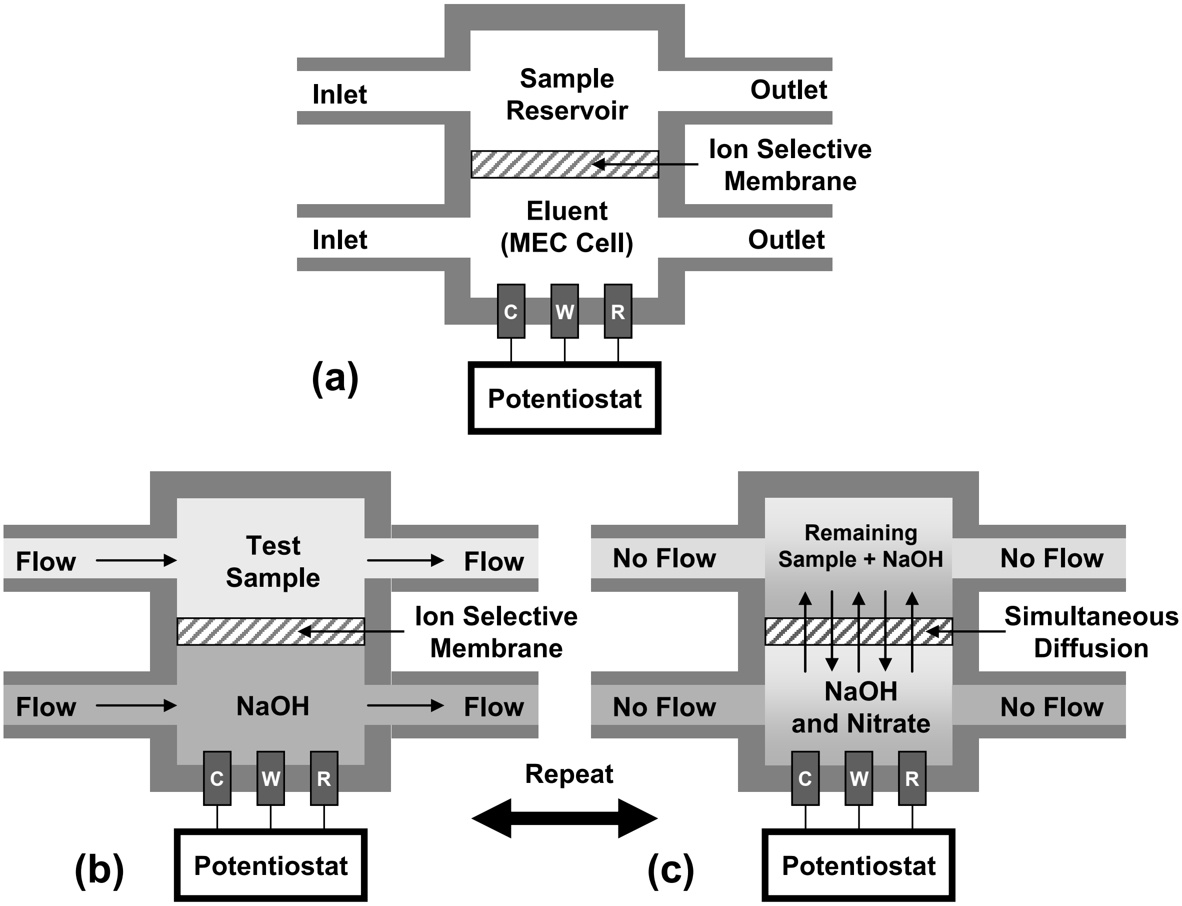

Figure 2. Schematic diagrams of the electrochemical-sensor system and its operation sequence (from a to c). The electrodes shown are: counter electrode (C), working electrode (W), and reference electrode (R).

By numerical simulation of the nonlinear differential equation given above (2), we calculate the time required to reach equilibrium. For our design, equilibrium is reached in ~5 minutes. A Tokuyama ACS (Tokuyama Corp., Japan) membrane was selected and tested for the sensor system. The parameters used for our simulation were obtained from published research [6]. The selective transport of ions through such a membrane provides the selectivity needed for nitrate-specific measurements.

III. FABRICATION

A microfabrication process was used to produce microelectrodes with integrated microfluidic channels (Figure 3) on a substrate. The MEC cell has a silver working electrode patterned on a silicon-dioxide substrate. To simplify fabrication, the reference electrode was made of silver that is electrochemically anodized in 10-mM NaOH to form silver oxide. The counter electrode was made of platinum. The metal electrodes are deposited using a CHA e-beam evaporator. Titanium was used as an adhesion layer instead of chromium since it is not electrochemically etched during measurements. The surface area of each electrode is: silver working electrode 0.8×10^{-3} cm^2, platinum counter electrode 4.188×10^{-3} cm^2, and silver/silver oxide reference electrode 1.103×10^{-3} cm^2. A pair of 180-μm-deep microchannels are formed using deep reactive-ion etching (DRIE). A SEM image of the concentric electrodes and the microchannels are shown in Figure 4. The microsensor chip is then assembled into a sensor unit with the anion-permeable membrane and EDPM (ethylene-propylene-diene-methylene) rubber plates that define the reservoir and fluidic ports sized to accept standard connectors (Figure 5). The completed and assembled sensor unit is shown in Figure 6.

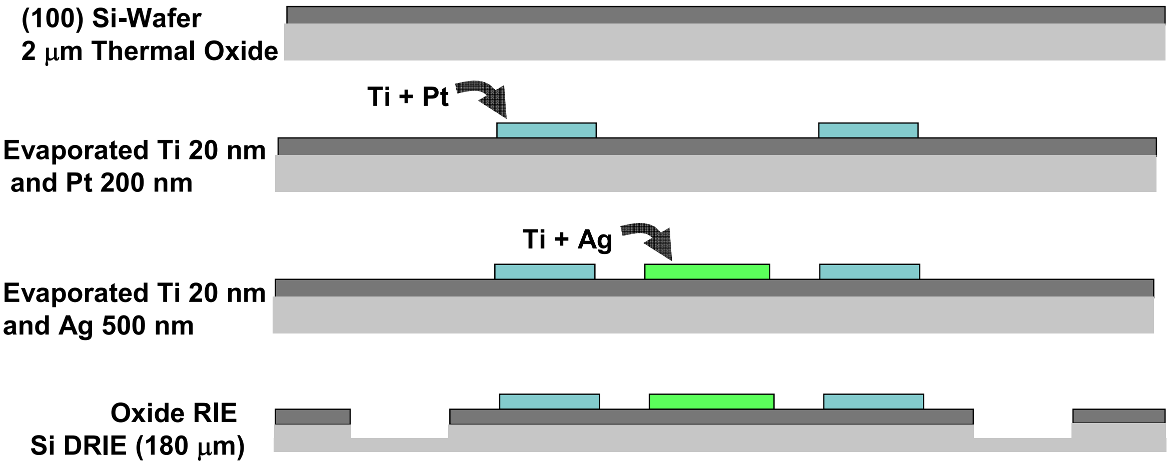

Figure 3. Fabrication process for the sensing chip.

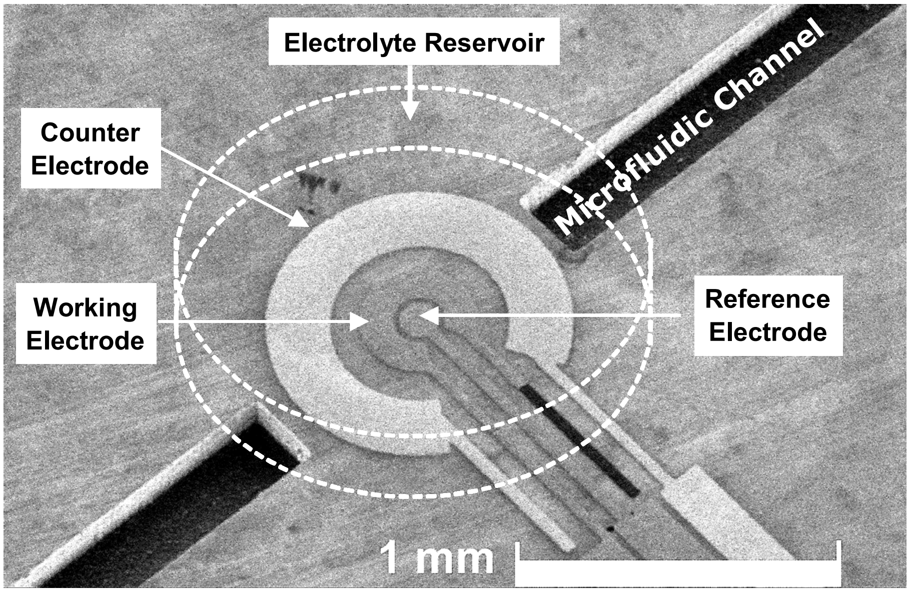

Figure 4. SEM image of the micromachined electrodes and the 180-µm-deep microchannels in the substrate. The working electrode is silver, the reference electrode is silver/silver oxide, and the counter electrode is platinum.

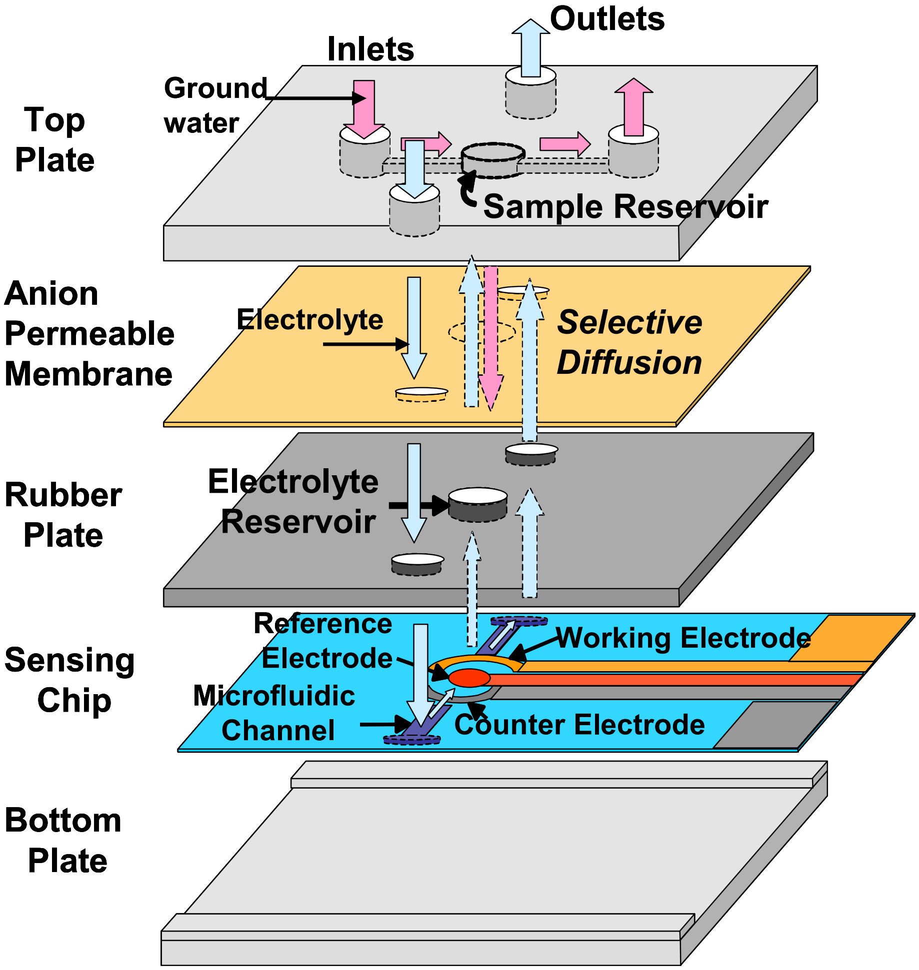

Figure 5. Exploded schematic diagram of the complete sensor unit.

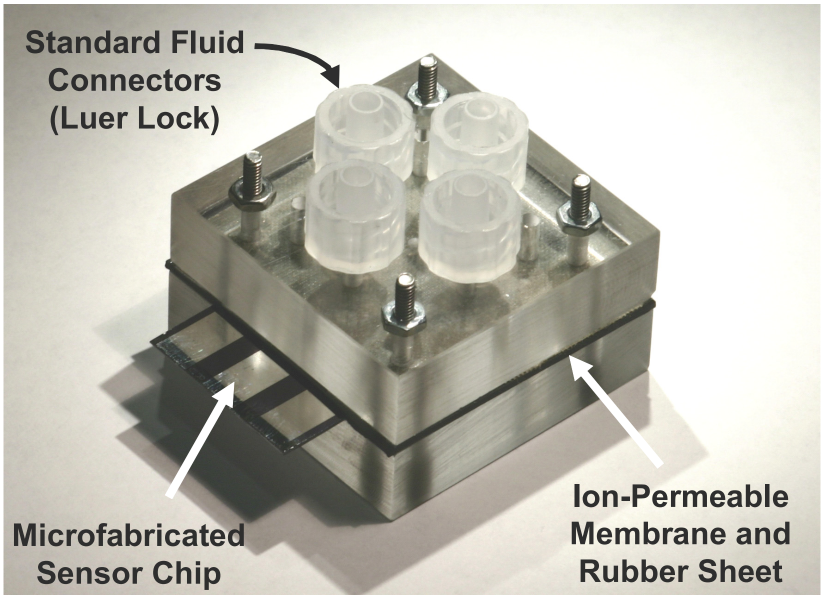

Figure 6. Assembled sensor unit with standard fluidic connectors.

IV. EXPERIMENTAL RESULTS

All solutions are made freshly from ultra-pure DI water and analytical reagent-grade chemicals. Also, analytical-grade commercial nitrate standards are used to obtain the calibration curves. The electrochemical apparatus consists of a CH Instrument 660B Electrochemical Workstation, a CHI 200 Picoamp Booster, and a PC for data acquisition and potentiostat control. The complete experimental bench-top setup is shown in Figure 7.

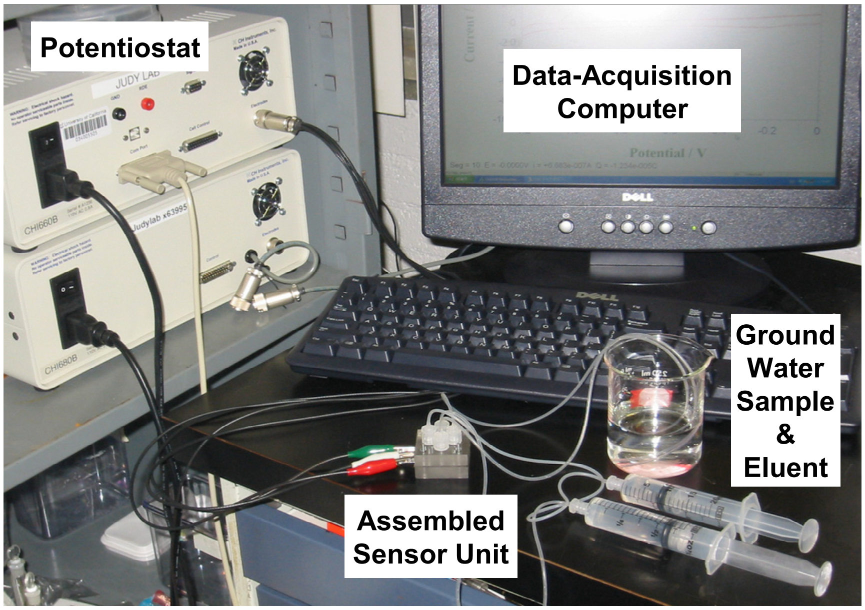

Figure 7. Photograph of the bench-top experiment (complete with the assembled sensor unit, test sample and electrolyte, potentiostat, and data-acqusition computer).

In order to obtain repeatable and sensitive measurements, the working electrode needs to be electrochemically activated before analysis [7]. This is done by sweeping the potential 20 times from -1.2 V to 0.8 V vs. Ag/AgCl, at a sweep rate of 1 V/s. Calibration curves for nitrate were obtained using chronocoulometry (Figure 8), in which the working electrode is biased at -0.85 V vs. Ag/AgCl and the nitrate reduction current is integrated for 0.5 s. With standard addition methods (1, 2, 5, 10, 20, 50, 100, 200, 500, 1000 μM nitrate), the integrated current (charge) is plotted with respect to concentration and the slope is calculated with linear regression. The calibration curves shown in Figure 8 represent the greatest and the least slope for the sensing chips tested. The data also illustrates the linearity (r^2) of our amperometric method. The detection limit of the microsensors is ~1 μM of nitrate.

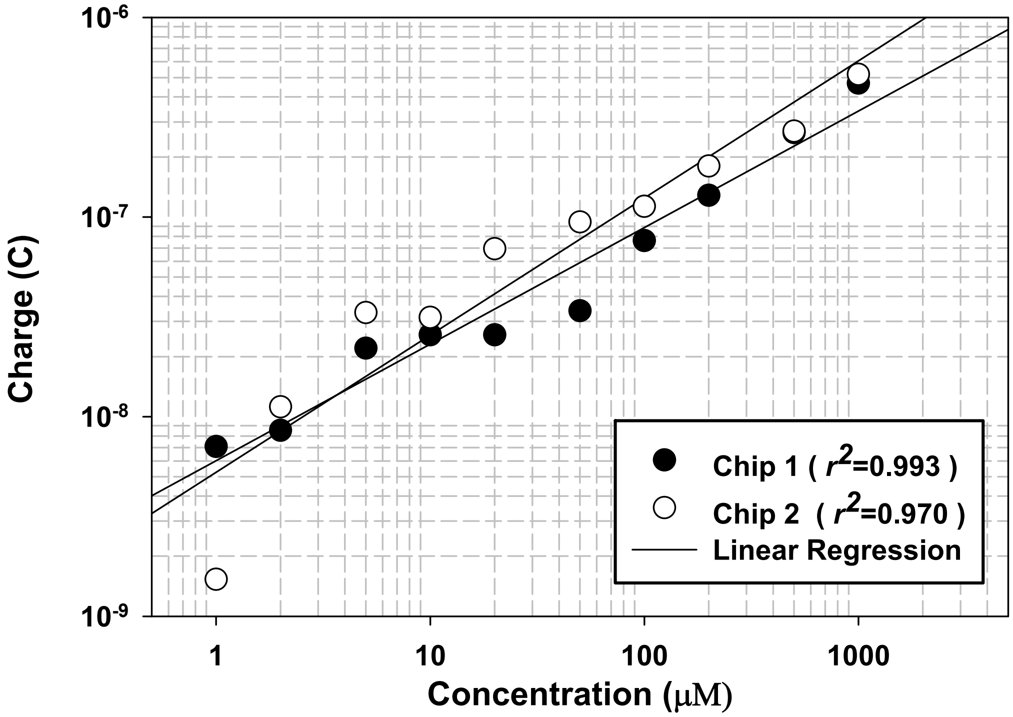

Figure 8. Calibration curves for the nitrate-sensor system that exhibit a minimum detection level of ~1 μM.

In order to examine the selectiveness of our microsensor, its response to 100-μM nitrate in a mixture of typical interfering ions in ground water (i.e., 100 μM each of PO_4^{-2}, SO_4^{-3}, F^-, Cl^-) was measured. The sensor output in response to such a mixture is only 13.9% higher than the average response for 100-μM nitrate (i.e. without interfering ions). Such a change in the output is small, compared to the 400% increase in total concentration in the mixture.

IV. CONCLUSIONS

By incorporating amperometric detection techniques, an anion-permeable membrane, and MEMS-fabrication techniques, we successfully demonstrated the feasibility of using a microsensor system to monitor nitrate concentration in ground water. The performance of the nitrate microsensor is sufficient for this application (i.e., detection range from 1 μM to 1 mM with good selectivity). Long-term qualification tests are presently underway. Once integrated with a chip-scale potentiostat, miniature pumps, check valves, and a wireless sensor node, we anticipate that a revolutionary instrument for nitrate monitoring in water systems could be realized.

ACKNOWLEGEMENTS

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