

## Micromachined Amperometric Nitrate Sensor with an Anion Permeable Membrane

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Nitrate is considered to be a major contaminant in ground-water and surface-water systems, and can present significant risk to human health and the environment. Consequentially, federal health and environmental agencies, ecological scientists, and environmental engineers have a great need for small, low-power, reliable, and yet sensitive nitrate sensors that can be remotely operated. Compared to commercially available nitrate-sensing systems (e.g. ion chromatography, spectrometry, and electrophoresis), electrochemical measurements (e.g., amperometry and potentiometry) are relatively simple, easily miniaturizable, low power, and yet sensitive enough for the targeted applications ( $\sim 1 \mu\text{M}$  to  $10 \text{mM}$ )[1].

Selectivity is a major concern in electrochemical measurements. Our sensors achieve selectivity using a nitrate-ion-permeable membrane (ACS, Tokuyama Corp.) originally produced for drinking water dialysis [2]. A schematic diagram of the sensing system and an illustration of its operation are shown in Figure 1. The sample reservoir is filled with a ground-water test sample and the microelectrochemical (MEC) cell is filled with an electrolytic eluent ( $10 \text{mM NaOH}$ ) (Figure 1, step1,2). Hydroxide ions diffuse across the permeable membrane due to a large concentration gradient while nitrate ions enter the cell by diffusion, maintaining charge balance. After equilibrium is reached ( $\sim 5$  minutes in our design), the measurements are performed (step3). Nitrate diffuses faster than the other interfering anions due to its larger diffusion coefficient in the membrane and this is how we entail selectivity.

To quantify nitrate concentration we used a silver working electrode, since silver exhibits a high activity for reducing nitrate to nitrite or ammonia [3,4]. To simplify fabrication, the reference electrode was made of electrochemically-anodized silver to form silver oxide. The counter electrode was made of platinum. The configuration and an SEM of the concentric electrodes and the microchannels are shown in Figure 1. The microsensor chip is then assembled into a sensor unit with the anion-permeable membrane and a set of plates (Figure 2). The plates are machined to define the reservoir and fluidic ports, which are sized to accept standard connectors (Figure 3).

A calibration curve for sample measurement (Figure 4) is obtained using chronocoulometry, in which the working electrode is biased at  $-0.85 \text{V vs. Ag/AgCl}$ . The integrated current (charge) is plotted with respect to concentration and slopes are calculated with linear regression. The calibration plot shown represents the greatest and smallest slopes of the sensing chips tested. The detection limit of the microsensor is  $\sim 1 \mu\text{M}$  of nitrate. In order to examine the selectiveness of our microsensor, its response to a mixture of typical interfering ions in ground water ( $\text{PO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $100 \mu\text{M}$  each) and  $100\text{-}\mu\text{M}$  nitrate was measured. The sensor output is only 13.9% higher than the average response for  $100\text{-}\mu\text{M}$  nitrate-only samples.

### References

- [1] M.J. Moorcroft et al., *Talanta*, vol. 54, pp. 785, 2001.
- [2] H. Miyoshi, *J. Membrane Sci.*, vol. 141, pp. 101, 1998.
- [3] M. Fedurco et al., *J. Echem. Soc.*, vol. 146, no. 7, pp. 2569, 1999.
- [4] S. Cattarin, *J. Appl. Echem.*, vol. 22, pp. 1077, 1992.

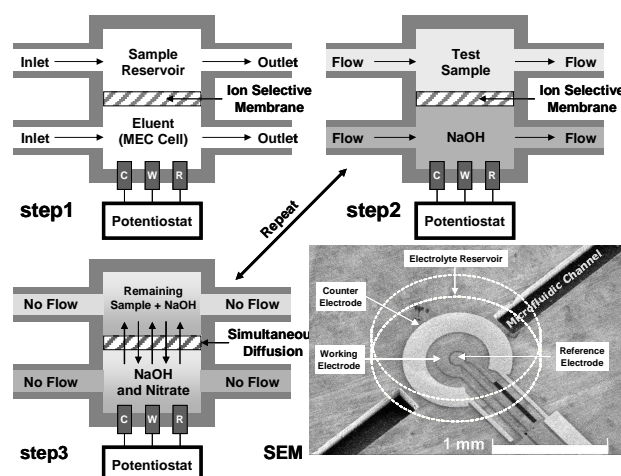


Figure 1. Schematic diagrams and a SEM of the electrochemical-sensor system

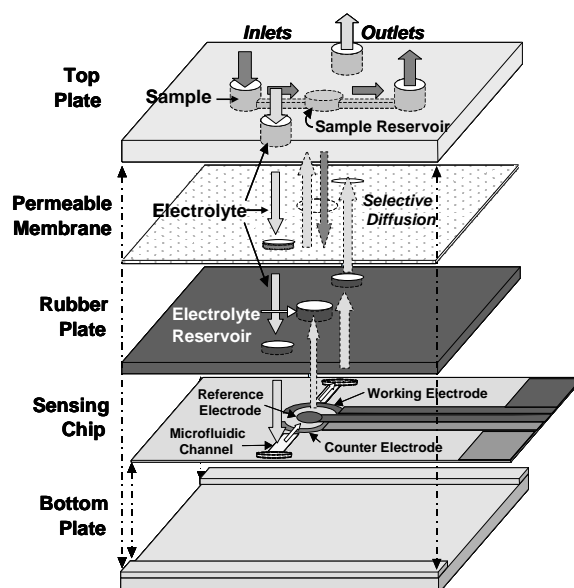


Figure 2. Exploded schematic diagram of the complete sensor

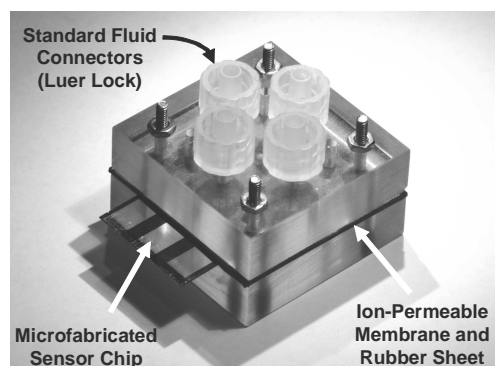


Figure 3. Assembled sensor unit with standard connectors unit.

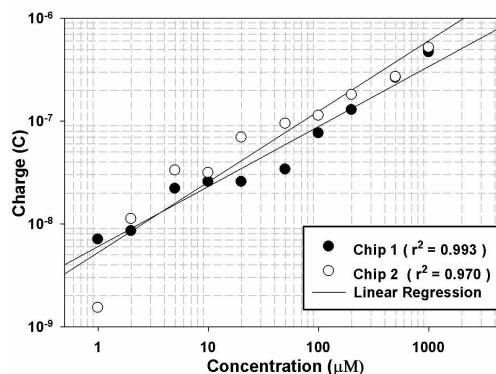


Figure 4. Calibration curves for the nitrate-sensor system with a minimum detection level of  $\sim 1 \mu\text{M}$ .