

AIR-GAP FIBER-OPTIC AMMONIA GAS SENSOR

SATYAJIT KAR and MARK A. ARNOLD*

Department of Chemistry, University of Iowa, Iowa City, IA 52242, U.S.A.

(Received 1 August 1992. Revised 14 August 1992. Accepted 11 September 1992)

Summary—A novel fiber-optic gas sensing arrangement based on an air-gap design is evaluated. In this arrangement, a small gap of air separates the internal solution from the sample. In addition, a second air-gap separates the internal solution from a fiber-optic probe which measures the fluorescence of the internal solution. A series of gas sensors for ammonia is used to investigate several critical design parameters. The length of the air-gap between the internal solution and the fiber-optic probe affects the magnitude of response. The length of the air-gap separating the internal and sample solutions has minimal effect on either magnitude or rate of response. As with membrane-type gas sensors, thickness of the internal solution and concentration of the indicator dye are the most important sensor parameters to consider when designing a fiber-optic gas sensor.

Fiber-optic ammonia sensors capable of nanomolar detection have been developed and the use of these devices to investigate neurochemical events has been proposed.¹ The utility of such a device for biomedical research depends to some extent on the dimensions of the sensing tip. Smaller sensing tips will permit greater spatial resolution, thereby enhancing the information content of the measurement.

Ammonia gas sensing electrodes based on potentiometric pH detection have been miniaturized with tip sizes as small as 10 microns.^{2,3} An air-gap design was used to fabricate these sensors. The air-gap is constructed by silanizing a short region inside a drawn out glass capillary. Sensor construction is completed by placing a small volume of internal solution above this hydrophobic region and then positioning a small pH/reference electrode pair in the internal solution. Additionally, the corresponding micro-biosensors have been demonstrated by covalently attaching urease to the outer surface at the tip of the glass capillary.⁴

We have characterized a series of miniature fiber-optic ammonia sensors based on this same air-gap design. Instead of using a pH electrode to measure the pH of the internal solution, a set of optical fibers is used in combination with a fluorescent pH indicator dye. Our intention has been to identify sensor parameters that most strongly influence the analytical characteristics of air-gap fiber-optic gas sensors. Sensors

with tip sizes from 0.2 to 0.5 mm have been constructed. The sensor design parameters considered in this investigation include the positioning of the internal solution relative to both the optical fibers and the sample solution, volume and length of the internal solution, and concentration of the indicator dye.

EXPERIMENTAL

Sensor fabrication

Sensor bodies were constructed from glass capillary tubes (Kimble Products, Skokie, IL) in the following manner. First, the closed end of the tube was removed and then the tube was cleaned by placing it into boiling water for approximately 30 min followed by a thorough rinsing with water. Cleaned capillaries were dried in a 115° oven. Sensing tips were formed by drawing out the capillary when the glass became red-hot under a normal gas flame. In this way, two sensor bodies were produced from each capillary with tip sizes ranging from 0.2 to 0.5 mm. Tips were silanized individually by dipping each into a 4% solution of dichlorodimethyl silane in carbon tetrachloride. The solution that occupied the tip was allowed to evaporate in air. Each tip was dipped between 6 and 10 times and the treated tips were placed in an 80° oven for 1 hr. Silanized tips were stored under nitrogen.

Sensors were constructed by placing a small volume of the internal solution inside a sensor

*Author for correspondence.

body between the silanized region and a fiber-optic probe. Figure 1 shows the sensor tip schematically. The fiber-optic probe was constructed by packing four plastic optical fibers (Super Eska type EK-10 fibers from Mitsubishi Rayon America, New York, NY) into a narrow bore glass capillary. This capillary fit snugly in the sensor body by matching the outer diameter of the capillary with the inner diameter of the untreated end of the sensor body. The optical fibers were held in the inner capillary with an adhesive sealant. A needle was used to place a small volume of the internal solution in position. The fiber-optic probe was then placed in the sensor body until its tip butted against the tapered portion at the drawn tip. A low temperature dental wax (Sybron-Kerr, Romulus, MI) was used to seal the top of the sensor and to hold the fiber-optic probe in place. As illustrated in Fig. 1, there was a short gap between the internal solution and the tip of the fiber-optic probe. As specified below, several internal solution compositions were used throughout this investigation. Internal solution volumes were calculated from differential weights obtained by weighing the sensor body before and after placement of the internal solution.

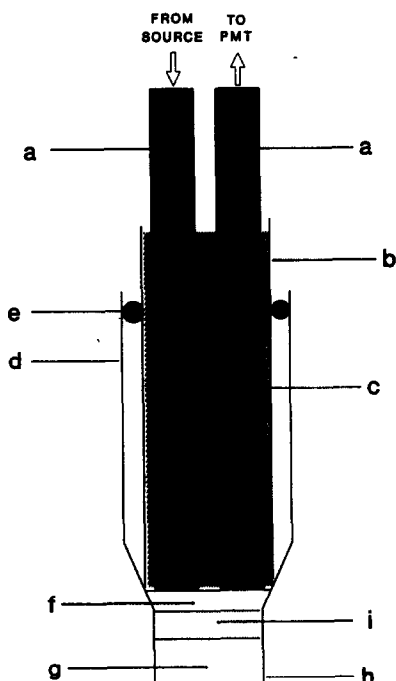


Fig. 1. Schematic representation of the air-gap fiber-optic ammonia sensor showing a, optical fibers; b, fiber-optic probe body; c, epoxy; d, gas sensor body; e, wax seal; f, air-gap; g, air-gap; h, sensor tip; i, internal solution.

Fluorescence measurements

Fluorescence from the internal solution was measured through the fiber-optic probe by using an instrumental arrangement similar to that reported previously.¹ Basically, the incident radiation was selected from a 100 watt tungsten halogen lamp by a 490 nm narrow band pass filter and then launched into two of the four plastic fibers of the fiber-optic probe. Emission was collected by the remaining fibers and directed toward the detection optics which consisted of a 540 nm interference filter and a photomultiplier tube (PMT).

Sensor calibrations

Sensors were calibrated by immersing the sensor tip in a 10.0-ml aliquot of a 0.01M sodium hydroxide solution that contained 0.105M sodium chloride. The required levels of ammonia were obtained by adding a series of microliter additions of an ammonium chloride standard solution. The steady-state sensor response was recorded after each change in the ammonia concentration. Response times were measured as the time required to achieve 95% of the final steady-state response.

Reagents

Both 5(and 6)-carboxyfluorescein (CF) and 5(and 6)-carboxy-4',5'-dimethylfluorescein (CDMF) were used as received from Molecular Probes, Inc., Eugene, OR. All other reagents were analytical grade quality and were purchased from common suppliers. Freshly distilled-deionized water from a Milli-Q three house purification unit was used for all solutions.

RESULTS AND DISCUSSION

The position of the internal solution is a critical parameter in terms of both the magnitude and rate of sensor response. A small air gap between the fiber-optic probe and internal solution was found to be necessary to prevent the internal solution from climbing between the outer wall of the fiber-optic probe and the inner wall of the sensor body (see Fig. 1).

The size of gap between the fiber-optic probe and internal solution has important optical consequences in terms of both the intensity of the incident radiation hitting the internal solution and the efficiency of the fibers to collect the emitted radiation. Both parameters are

adversely affected by increasing this distance. As a result, a larger gap lowers the sensitivity of the measurement. For example, the effect of increasing the gap distance from 0.6 to 3.2 mm was measured for a sensor with an internal solution composed of 0.112M ammonium chloride and 1.0 μ M CF. In this experiment, the sensor response was measured for a zero to 10 μ M concentration step and the volume of the internal solution was 0.5 μ l throughout. The magnitude of response decreased approximately 4-fold when the gap distance was increased, yet there was no significant difference in sensor response times.

The position of the internal solution was unstable when the chamber holding this solution was not sealed (see Fig. 1). Slight changes in ambient atmospheric pressure caused movement in the internal solution, thereby altering the sensor response. Another problem encountered with unsealed sensors was evaporation of the internal solution. Evaporation affected the sensor response in two ways. First, a decrease in the volume of the internal solution resulted in an increase in the distance between the fiber-optic probe and the internal solution which altered the fluorescence measurement. Second, evaporation altered the sensor response by concentrating the components in the internal solution. The small volumes of internal solution resulted in rather dramatic evaporation effects which demanded sealing the chamber before reproducible responses could be obtained.

The length of the air-gap region at the sensor tip was less critical than the length of the internal solution. The length of the internal solution affects both the magnitude and rate of response. These effects are illustrated by the data plotted in Fig. 2 which presents both the

magnitude and rate of response measured for an ammonia concentration step from zero to 10 μ M. The internal solution used in this experiment was composed of 0.02M ammonium chloride and 10 μ M CF and the air-gap at the sensor tip was 3 mm. Increases in the length correspond to increases in the optical path length which provides higher sensitivity and larger responses. As the length approaches 2.5 mm, the response becomes insensitive to solution length, thereby defining the maximum optical path length in terms of the fluorescence measurement. Unfortunately, response times also increase as a function of solution length. Response times increased by a factor of 4.5 as the length was varied from 0.8 to 2.5 mm. Extrapolation to zero length gives the minimum response time based on the other parameters of the sensor design, most notably the length of the air-gap region. The effect of air-gap length was minimal when internal solution lengths ranged from 1 to 5 mm. Under these conditions, the rate of diffusion through the internal solution is rate limiting and controls the sensor response time. Similar results have been obtained for fiber-optic ammonia gas sensors with microporous Teflon membranes as the gas-permeable barrier.^{1,5}

Both the magnitude and rate of response are also strongly influenced by the concentration of the indicator dye. These effects were examined by recording responses for a zero to 10 μ M concentration step as a function of the concentration of CF. Besides the indicator, the internal solution contained 0.1M ammonium chloride. As has been observed for sensors with Teflon membranes,^{1,5} both the magnitude of response and response times increase as the dye concentration increases. By increasing the dye concentration from 2 to 10 μ M, the magnitude of the response increased by a factor of 2.5 and the response time increased from 4 to 11 min. Both effects are caused by a need for more ammonia to enter the internal solution to achieve equilibrium at higher dye concentrations.

Response curves for miniature air-gap fiber-optic ammonia sensors have the same non-linear shape as the larger, membrane-type sensors. Figure 3 provides a sample response curve for a sensor with approximately 0.3 μ l of an internal solution composed of 2.0mM ammonium chloride and 0.1mM CDMF. The curve shape matches that predicted by the response function which has been derived for fiber-optic ammonia sensors.^{5,6} Relative

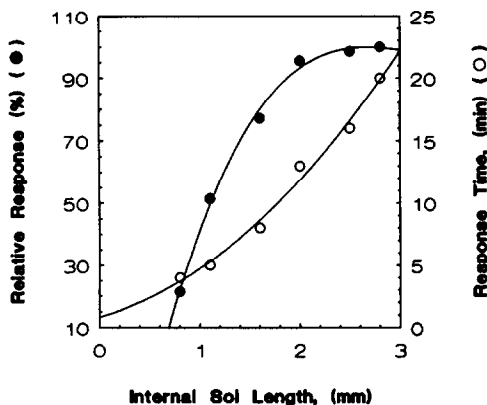


Fig. 2. Effect of internal solution length on the magnitude of response (right axis) and response time (left axis).

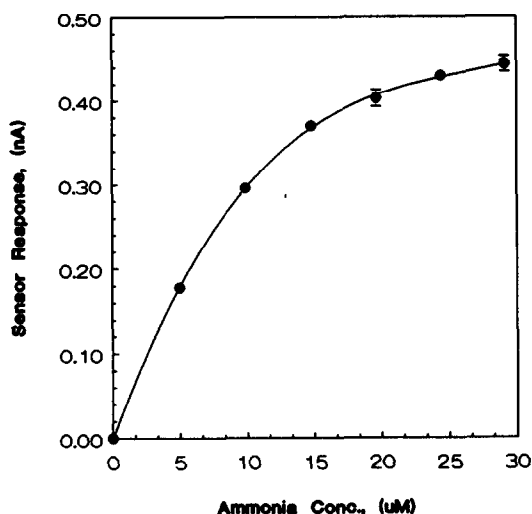


Fig. 3. Sample calibration curve for an air-gap fiber-optic ammonia sensor.

standard deviations for this sensor range were from 1 to 4% over the 5 to 30 μM concentration range. Response times varied from 3 to 10 min over this same concentration range with longer response times recorded at lower ammonia concentrations. The limit of detection was calculated to be 0.5 μM ($S/N = 3$) which is similar to that obtained for a membrane-based sensor with the same internal solution.

CONCLUSION

The response properties of fiber-optic ammonia sensors based on an air-gap design are similar to those for the larger, membrane-based sensors. The results of this investigation indicate that miniaturization is possible without adversely affecting the sensitivity, limit of detection or response time of the fiber-optic ammonia sensor. Overall, the thickness of the internal solution and the concentration of the indicator dye are the critical parameters that determine analytical performance.

Acknowledgements—This work was supported by grants from the National Science Foundation (BNS-8716769) and the National Institutes of Health (GM-35487).

REFERENCES

1. S. Kar and M. A. Arnold, *Anal. Chem.*, 1992, **64**, 2438.
2. C. P. Pui, R. F. Miller and G. A. Rechnitz, *ibid.*, 1978, **50**, 330.
3. J. P. Joseph, *Mikrochim. Acta*, 1984, **2**, 473.
4. J. P. Joseph, *Anal. Chim. Acta*, 1985, **169**, 249.
5. T. D. Rhines and M. A. Arnold, *Anal. Chem.*, 1988, **60**, 76.
6. M. A. Arnold and T. J. Ostler, *ibid.*, 1986, **58**, 1137.