Chemical Sensors for Hazardous Waste Monitoring

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ABSTRACT:

A family of novel fiber optic sensors is being developed for on-line monitoring of chemical species in gases and liquids. The sensors utilize porous polymer or glass optical fibers in which selective chemical reagents have been immobilized. These reagents react with the analyte of interest resulting in a change in the optical properties of the sensor (absorption, transmission, fluorescence). Using this approach, low parts per billion level detection of the aromatic fuel vapors, benzene, toluene and xylene, and hydrazines has been demonstrated, as have sensors for ethylene vapor. Also relevant to groundwater monitoring is the development of a pH Optrode System for the pH range 4-8, with additional optrodes for lower pH ranges.

INTRODUCTION

The functional operation of optical fiber chemical sensors involves the interaction of light which propagates through the fiber, with a reagent that in turn selectively interacts with the environment to be sensed. Typical optical properties including evanescent absorption and fluorescence, and chemiluminescence can be exploited in these sensors. The reagents are normally immobilized into a membrane or porous polymer matrix and then coated either on the tip or side of the fiber.

One of the problems encountered with fiber optic chemical sensors based on evanescent absorption is their characteristic low sensitivity. This results from the limited depth of penetration of the evanescent field of the light into the reagent cladding as well as the effect of internal reflections [1-4].

Figure 1 illustrates the principle of detection used in fiber optic chemical sensors. In the figure, porous glass and porous polymer approaches are compared to conventional evanescent chemical sensors. In the porous fiber, the analyte penetrates into the pores and interacts with the reagent which is previously cast (immobilized) into the pores. The porous fiber has a large interactive surface area (due to the large surface area provided by the pores), resulting in dramatically enhanced sensitivity in the optrode. Another advantage of a porous glass fiber is the small sensing region (about 0.5 cm in length and 250 microns in diameter). Additionally the sensor is an integral part of the fiber waveguide. This latter feature minimizes the complications associated with the physical and optical coupling of the sensor probe to data transmission fibers. In addition, multiple fiber sensors can be deployed using a single analytical interface unit. These sensors are expected to be less expensive than conventional fiber optic chemical sensors based on materials cost and ease of fabrication. Porous

fiber sensors for the measurement of humidity, pH, ammonia, ethylene, CO, hydrazines, and the aromatic fuel constituents benzene, xylene and toluene have been successfully demonstrated by GEO-CENTERS, and by Rutgers University [5-12].

Fabrication of Porous Glass Optical Fiber

Porous glass optical fibers are fabricated by the Fiber Optic Materials Research Program at Rutgers University, using the methodology described below [5].

The material used in the fiber is an alkali borosilicate glass with the components SiO_2, B_2O_3 and alkali oxides. This type of glass is a well characterized system, producible at a low cost. Most importantly it exhibits the phenomenon of liquid/liquid immiscibility within a certain temperature range. The above composition is melted in an electrical furnace at 1400°C and cast into rods with a 20 mm diameter and 0.5 m in length. The rods are drawn into fibers at about 700°C by a draw tower equipped with an electrical furnace. Fibers with a 250-300 micron diameter with a 5-10 cm length are then heat treated in a tube furnace at 600°C for about 3 hours. The heat treated glass becomes phase separated, with one phase silica rich and the other boron rich. The boron rich phase is leached out of the glass by placing the fiber in a bath of hydrochloric acid. The fibers are subsequently washed with distilled water and rinsed with alcohol. Figure 2 illustrates the processing steps for fabricating porous fibers.

Subsequent to fiber preparation, the porous segment is cast with the sensing reagent (indicator). This is done by dissolving the reagent in a solvent at a predetermined concentration and soaking the porous fiber in the solution. The reagent is then dried into the pores by air drying or in a low temperature oven. Alternatively, the glass surface can be treated with a silanizing reagent to facilitate chemical coupling to the sensing reagent.

Fabrication of Porous Polymer Optical Fiber

As an alternative to chemical immobilization or physical adsorption in porous glass, porous polymer optial fibers can also be used to create fiber optic chemical sensors. Sensors using these fibers have been demonstrated for ethylene, CO, NH_3, pH, and humidity detection. The principle of porous polymer fiber sensors has the same basis as porous glass sensors. Consequently high sensitivity is achieved. In this approach the indicator is dissolved directly into the monomer solution before forming the polymer fiber; therefore, the indicator is strongly bonded to the polymer network. In fact, the porous polymer approach provides the advantage of both chemical bonding and physical entrapping of the indicator. Also, the pore size and the amount of indicator can be precisely controlled by changing the composition of the monomer solution, resulting in very good sensor-to-sensor reproducibility. This fabrication process is additionally quite suitable for mass production. This reduces the cost of optrodes.

The porous polymer fibers are prepared by a heterogeneous copolymerization technique. The basic principle behind this technique is the polymerization of a mixture of monomers which can be crosslinked in the presence of an inert and soluble component solvent. Subsequent to polymerization, the inert solvent which is not chemically bound to a polymer network, is easily removed from the polymer leaving an interconnected porous structure.

Monomer starting solutions are prepared which contain the crosslinker, initiator, inert solvent and chemical indicator. The mixture, including the indicator, is injected into a length of glass capillary, (typically 500 microns in diameter). The filled glass capillaries are sealed such that they are virtually free of air, and polymerization is initiated and completed in a low temperature oven. After polymerization, the uniform and transparent polymer fibers are pulled out of the capillaries. Finally, the fibers

are washed in an organic solution to remove any remaining inert solvent.

A combination of parameters determines the final physical properties of the cross-linked polymer network. These include the solvent properties, amount and type of inert solvent, as well as the quantity of cross-linking agent employed.

Results and Discussion

Porous glass and porous polymer optrodes have been designed and demonstrated for aromatic fuel vapors (benzene, toluene, xylene), hypergol vapors (hydrazine and UDMH), for NH_3, CO and ethylene. Similarly, optrodes have been demonstrated for the chemical parameters pH, humidity and moisture content.

A pH Optrode System is currently under development which is applicable to a variety of field screening and contamination monitoring tasks. Porous glass pH optrodes have been fabricated which are operational in the pH 4-8 range. A unique co-immobilization technique was developed to tailor the sensor pH sensing range to a specific application. Optrodes are fabricated by first silanizing the porous fiber surface to facilitate the attachment of the sensitive indicator material. Spectral transmission scans are conducted in order to identify the wavelength region of maximum sensitivity to pH. The sensor interrogation wavelength is selected based on these spectral scans.

Optical intensity versus time measurements as a function of pH, have been made for each optrode at the interrogation wavelength. The sensitivity and linearity is determined by plotting optical intensity at equilibrium, versus pH. Figure 3 shows the response of the optrode with an immobilized indicator. The sensor is operational between pH 4 and pH 6.5, with greatest sensitivity and linearity between pH 4.5 and pH 6. Saturation of the sensor response occurs at pH values above 7 and less than 4.

A second indicator, which is structurally very similar to the first indicator, has been tested with the intent of increasing sensitivity at higher pH values. The response of this indicator is presented in Figure 4. The data indicates good linearity and sensitivity above pH 7.

A mixture of the two indicators was immobilized in a porous glass fiber. The results with this sensor are shown in Figure 5. The data indicates both excellent sensitivity and linearity across a pH range extending from 4 to 8. The co-immobilization of these two indicators represents a unique approach to sensor design and demonstrates that sensing range can be tailored to meet specific requirements.

The reversibility of these sensors has been evaluated. This is accomplished by cycling a test solution, into which the pH optrodes have been immersed, between pH values of 4.5 and 7.

Figure 6 depicts the variation in optical transmission of the pH optrode as a function of time. The data indicate that the sensor is fully reversible and peak to peak reproducibility is better than 90%. The spikes in the response curves are artifacts associated with the test setup. Similar results have been obtained using porous polymer optical fiber.

Fuel Vapor Optrodes

GEO-CENTERS, INC. has designed, fabricated and evaluated porous fiber optrodes for detection of aromatic fuel constituent vapors. A xylene optrode with sensitivity <50 ppb has been demonstrated. Response time, reproducibility, linearity, and selectivity have been determined. Benzene and toluene optrodes have also been demonstrated. Laboratory results indicate that there are highly sensitive optrodes, with near real time response. They are additionally capable of selective detection of target species.

With these optrodes (as well as the hypergol, ethylene, and CO optrodes) the rate of change of the optical transmission is directly proportional to analyte concentration. An example of xylene optrode response to different xylene concentrations is presented in Figure 7. Each curve corresponds to a different xylene concentration. A plot of the slopes of the data in Figure 7 versus xylene concentration is shown in Figure 8. This data demonstrates good sensor linearity from low part per billion to low part per million concentrations.

Hypergolic fuel optrodes have been developed to detect vapors for NASA and U.S. Air Force operation applications.

The principle of operation and sensor response is similar to that of the xylene optrodes. The hypergolic fuel optrodes can be configured as personal dosimeters for industrial hygiene applications or as portable detection instruments. Figure 9 shows a typical optrode response as a function of time for different concentrations of hydrazine. The slope of the optical intensity versus time curve may be correlated to the hydrazine vapor concentration.

Conclusions

Sensors utilizing optical waveguides offer many advantages for hazardous waste monitoring applications including size, near real time response, and low manning and expertise requirements. Additionally, porous glass and polymer optical fibers offer significant advantages in these applications because their large interactive surface area dramatically improves sensitivity. They also provide a continuous optical path. This minimizes mechanical and optical coupling losses. Additionally, sensor interfaces can be developed that allow multi-sensor operation. These chemical optrodes can be applied in a variety of environmental monitoring scenarios, as well as to developmental bioreactors, control of process streams, and industrial hygiene. A family of fiber optic optrodes offers the possibility of effectively having a wet chemistry laboratory that can be brought to the field.

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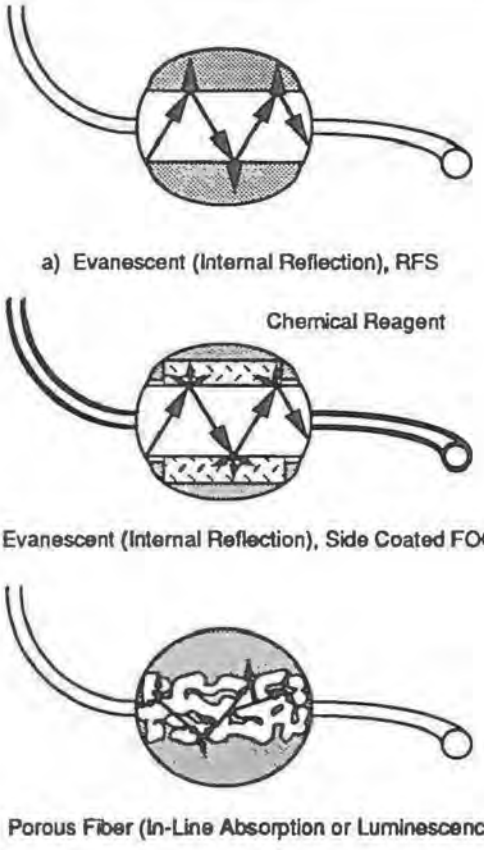

Figure 1.
Schematic Diagram Comparing Basic Sensor Designs

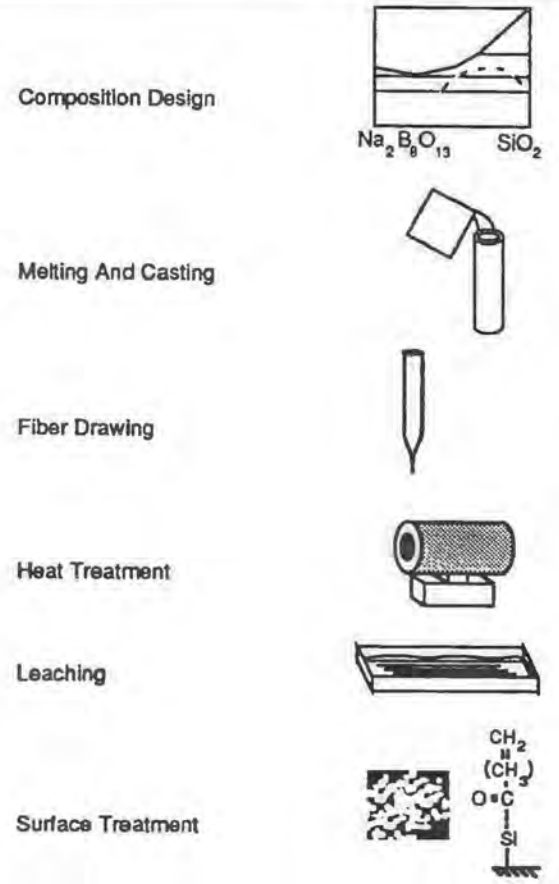

Figure 2.
Processing Steps For Producing Porous Glass Fibers

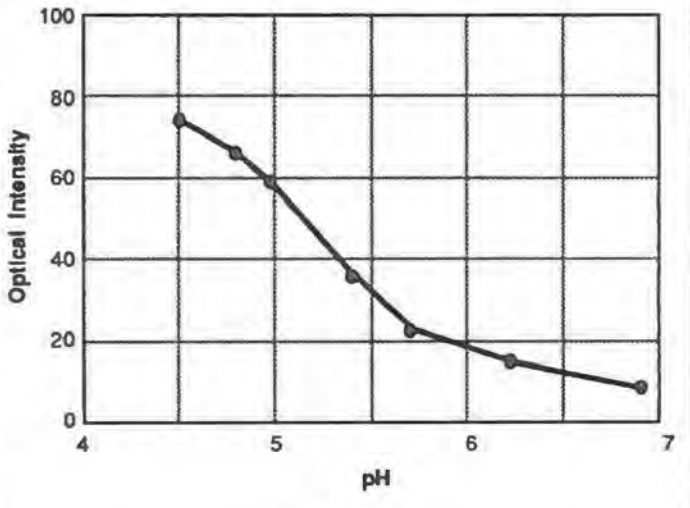

Figure 3.
Sensor Response With Bromocresol Green Indicator As A Function Of pH

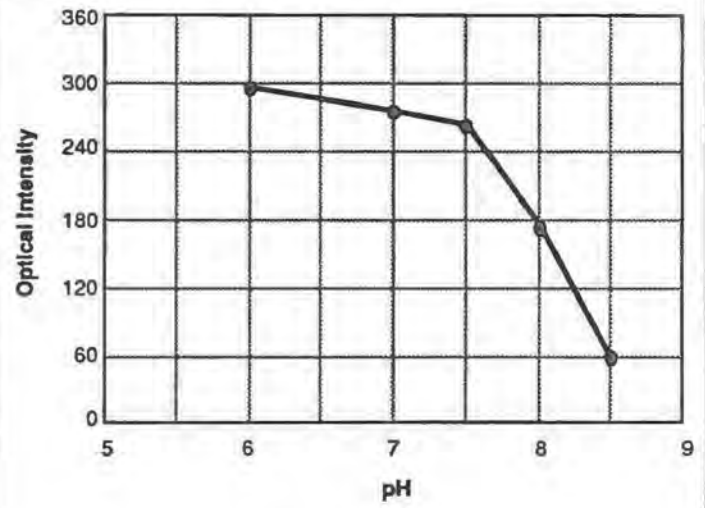

Figure 4.
Sensor Response With Bromocresol Purple Indicator As A Function Of pH

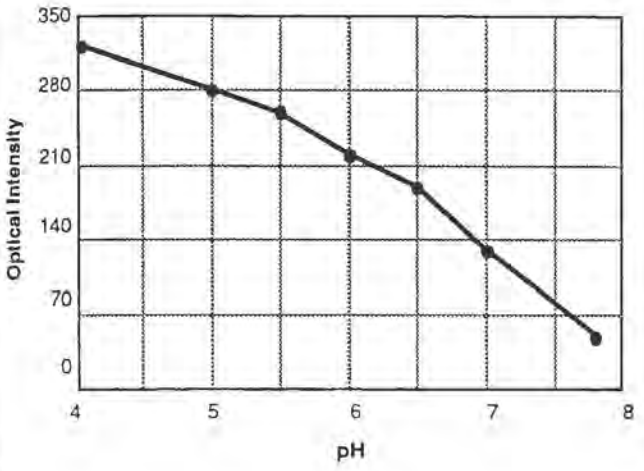

Figure 5.
Sensor Response With Co-immobilized Indicators As A Function Of pH

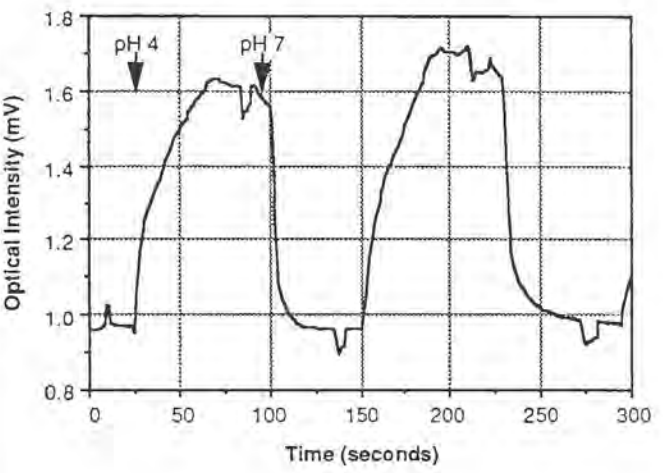

Figure 6.
Optrode response time as a function of pH

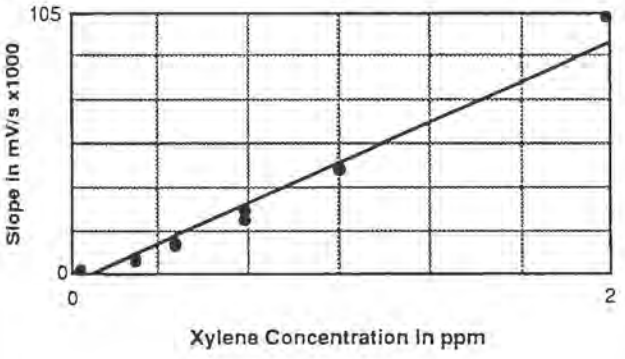

Figure 8.
Calibration Curve for Xylene Optrode Based onPorous Glass Fiber

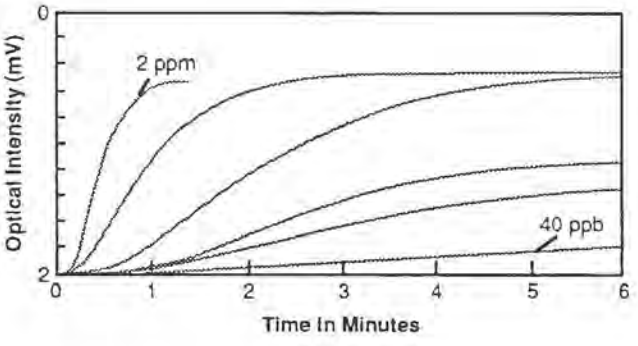

Figure 7.
Response Curves for Porous Glass Xylene Sensor. Xylene Concentrations Range from 2 ppm to ~40 ppb

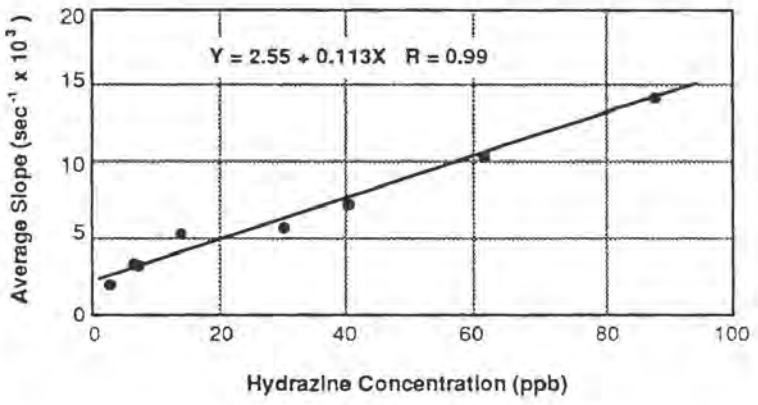

Figure 9.
Optrode Response to Hydrazine Vapor at 32% relative Humidity and 24 °C

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