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AROMATIC HYDROCARBON OPTRODES FOR GROUND-WATER MONITORING APPLICATIONS

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Research documented in this report produced a fiber-optic sensor utilizing a porous optical waveguide. This offered the advantage of improved sensitivity and specificit by impregnating fiber with a chemical indicator whose optical transmission properties change in the presence of aromatic species. The concept was adequately demonstrated the laboratory and a prototype optrode was developed which was sensitive for aromatic hydrocarbons to 50 ppb. The basic concept was proven.

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PREFACE

This report was prepared by GEO-CENTERS, INC., 7 Wells Avenue, Newton Centre, MA 02159, under Contract No. F08635-88-C-0257, for the Air Force Engineering and Services Center (AFESC), Suite 2, 139 Barnes Drive, Tyndall Air Force Base, Florida 32403-5319. The work was performed between September 1988 and February 1990. The AFESC project officer was Bruce Nielsen.

This final report describes the design, development and evaluation of fiber-optic-based optrode sensors for the in situ monitoring of groundwater and soil for aromatic hydrocarbons. The report focuses on the design and development of novel porous optical waveguides. In this approach the porous section of fiber is impregnated with a chemical indicator whose optical transmission properties change in the presence of aromatic species, providing a high degree of specificity.

This technical report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service, where it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for publication,

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SECTION I

INTRODUCTION

This final report summarizes the results of the Phase I SBIR project entitled "Aromatic Hydrocarbon Optrodes for Groundwater Monitoring Applications". The multiphase program was undertaken to design, develop, and evaluate fiber-optic-based optrodes (sensors) suitable for in situ monitoring of groundwater and earth material for the presence of aromatic hydrocarbons. In particular, an optrode is being designed using novel porous optical waveguides. Porous waveguides are prepared by heat treating and acid leaching of borosilicate optical fibers. Porous waveguides offer the advantages of greatly increased interactive surface area, which dramatically improves sensitivity, and a continuous optical path, thereby, eliminating mechanical and optical coupling losses. The porous section of fiber is impregnated with a chemical indicator whose optical transmission properties change in the presence of aromatic species, providing a high degree of chemical specificity.

In the Phase I effort concept feasibility was successfully demonstrated by designing and evaluating in the laboratory a fiber optrode sensitive to aromatic hydrocarbon vapor. The preprototype optrode has been characterized with the following demonstrated achievements:

- sensitivity to < 50 ppb
- response time < 1 minute
- excellent reproducibility and linearity
- specificity for aromatic fuel constituents

SECTION II

EXPERIMENTAL

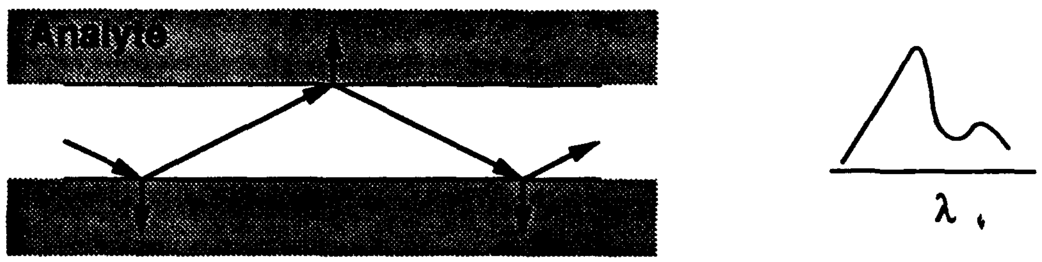
Presented are subsections on Porous Fiber Technology (II.A), Indicator/Analyte Systems (II.B), and Experimental Set-up (II.C). Results are presented in Section III, followed by Conclusions and Recommendations for further studies in Section IV.

A. POROUS FIBER TECHNOLOGY

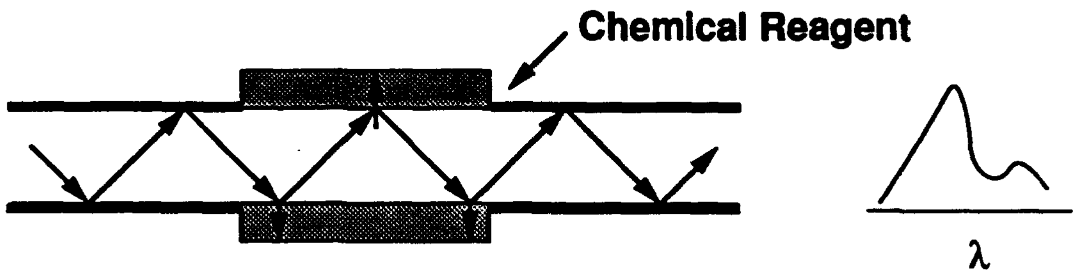
The use of optical fibers as components of chemical sensors for in situ monitoring of different chemical species is a recent development. The general approach in these sensors involves the interaction of light which propagates through the fiber interacting with a reagent that, in turn, selectively interacts with the environment to be sensed. The typical optical properties monitored include evanescent absorption and fluorescence, and chemiluminescence. 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 low sensitivity due to the limited depth of penetration of evanescent light into the reagent cladding, References 1-4.

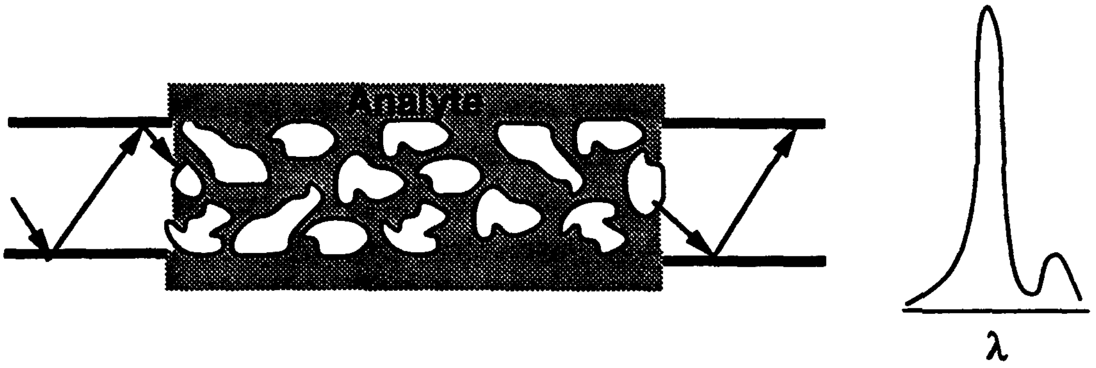
As part of the Phase I effort, a high sensitivity chemical sensor employing porous glass fibers was designed and developed. Figure 1 illustrates the principle of detection for a porous glass fiber sensor compared with a conventional evanescent sensor. In a typical evanescent fiber-optic sensor, the sensitivity is limited



a) Evanescent (Internal Reflection), RFS



b) Evanescent (Internal Reflection), Side Coated FOCS



c) Porous Fiber (In-Line Absorption or Luminescence)

Figure 1. Schematic Diagram Comparing Basic Sensor Designs

both by the depth of penetration of evanescent light into the reagent coated on the fiber core, and the number of internal reflections. In a porous fiber, the analyte penetrates into the pores and interacts with the reagent which is previously cast into the pores. Since the porous fiber has large surface area, the absorption is enhanced dramatically, leading to the high sensitivity of the optrode. Another advantage with a porous glass fiber is the small sensing region (about 0.5 cm in length and 250 microns in diameter) which is an integral part of the fiber waveguide. This latter feature eliminates the complications associated with the physical and optical coupling of the sensor probe to the fiber. In addition, multiple fiber sensors can be deployed from a single analytical unit and are expected to be less expensive than conventional sensors based on materials cost and ease of fabrication.

1. Fabrication of Porous Glass Fibers

The porous optical fibers used for this program were fabricated by Dr. Mahmoud Shahriari of the Fiber Optic Materials Research Program at Rutgers University. Dr. Shahriari also served as consultant on this effort. The methodology developed by Dr. Shahriari, Reference 5, is described below.

The material used in the fiber is an alkali borosilicate glass with the composition SiO_2, B_2O_3 and alkali oxides. This type of glass is a well characterized system, producible at a low cost and 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 and several meters long are produced this way. A portion of fiber (about 5-10 cm in length) is then heat treated in a tube furnace at 600°C for about 3 hours. At this point the heat treated glass is phase separated, 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 the fiber preparation, a porous segment (typically <1 cm) 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 heating the fiber in a low temperature oven.

Porous fiber sensors for the measurement of humidity, pH, ammonia, and CO have been successfully demonstrated, References 5-8.

B. INDICATOR/ANALYTE SYSTEMS

The simple aromatic components of fuel, such as benzene, toluene, ethylbenzene and xylene (BTEX) are quite stable by virtue of resonance electron effects, and the modest electron donating or withdrawing capability of the methyl ($-CH_3$) substituents. A number of indicator solutions were tested for room temperature response to the simple aromatics (in both the vapor and liquid state).

The indicators tested included tetracyanoquinodimethane (TCNQ), fluorescein, $AgNO_3$, (and $AgNO_3$ "mirror" solution), maleic anhydride, I_2 and tetracyanoethylene (TCNE). There is evidence

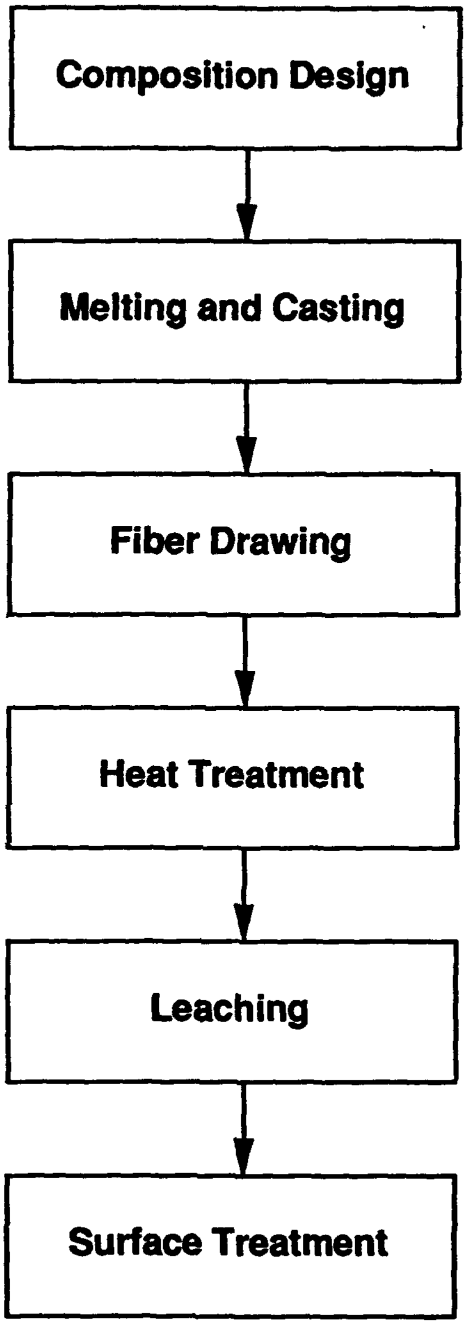


Figure 2 . Processing Steps for Producing Porous Glass Fibers

that the aromatics will form π-type complexes, or adducts with the latter three species, Reference 9. In this case the aromatic is considered a π-base, and the maleic anhydride, I_2 or TCNE is the π-acid. Only the I_2 and the TCNE formed complexes which exhibited a visible color change upon complexation. The iodine-benzene adduct produces a color change in the visible, but is limited practically by the volatility, and ready sublimation, of the I_2 reagent.

TCNE $[(CN)_2\ C = C(CN)_2]$ forms colored complexes with benzene, toluene and xylene which progress from yellow to reddish-orange, respectively. The complexes are believed to be 1:1 adducts in which the species lie parallel to one another. This would ensure maximum overlap of the π-molecular orbitals of the components. In solution, the adducts exhibit broadband absorption with peaks from 384nm to 460nm.

O-xylene was chosen as the target aromatic species for sensor characterization and evaluation *because of its strong* complex formation with TCNE, Reference 9, and an adduct absorption peak which overlaps well with the inherent transmission properties of the optical fiber (optical transmission in silica fiber falls off in the near UV).

The TCNE concentrations used in our experiments varied from .5 mg/ml to 10 mg/ml in dichloromethane. In the early experiments acetone was used as the solvent; this solution had a faint yellow color and turned black upon standing a few days. This may be explained by the formation of a competitive TCNE/solvent complex, Reference 10. No such stability problems were encountered when using dichloromethane as the solvent. Indicator solutions could be used for at least a week with no compromise in data reproducibility. Throughout this report the term "sensor" or "optrode" refers to a porous fiber section which has been cast with the TCNE indicator.

C. EXPERIMENTAL SET-UP

A schematic of the optical system and test bed is shown in Figure 3. The porous sensor is housed in a glass or brass tube, with holes drilled to admit the fiber. The fiber is held in place with an optically inactive adhesive. Sections of porous fiber, ~2.5cm in length, were cleaved from the longer sections provided by Rutgers. These were examined under a microscope to check the optical injection surfaces. Shorter regions (~0.5-1cm in length) were then made into sensing regions by treatment with the indicator.

The light source is a 100 W tungsten-halogen lamp (typically operated at 70 W), which is focused into an externally controlled Jarrell-Ash monochromator for wavelength selection and rapid scanning of the relevant spectra. The monochromatic light is chopped at a reference frequency (2005 Hz), focused with a microscope objective and launched into the sensing fiber. The transmitted light is detected by a silicon photodiode, coupled to a lock-in amplifier and computer controlled data acquisition system.

Most of the light launched into the fiber interacts with the indicator or other chemical reagents introduced into the waveguide. "In-line" optical absorption occurs and is very strong, as in the case of a long pathlength absorption cell. Light loss due to scattering by the porous glass host is approximately .7dB/cm which, does not compromise sensitivity over such short lengths.

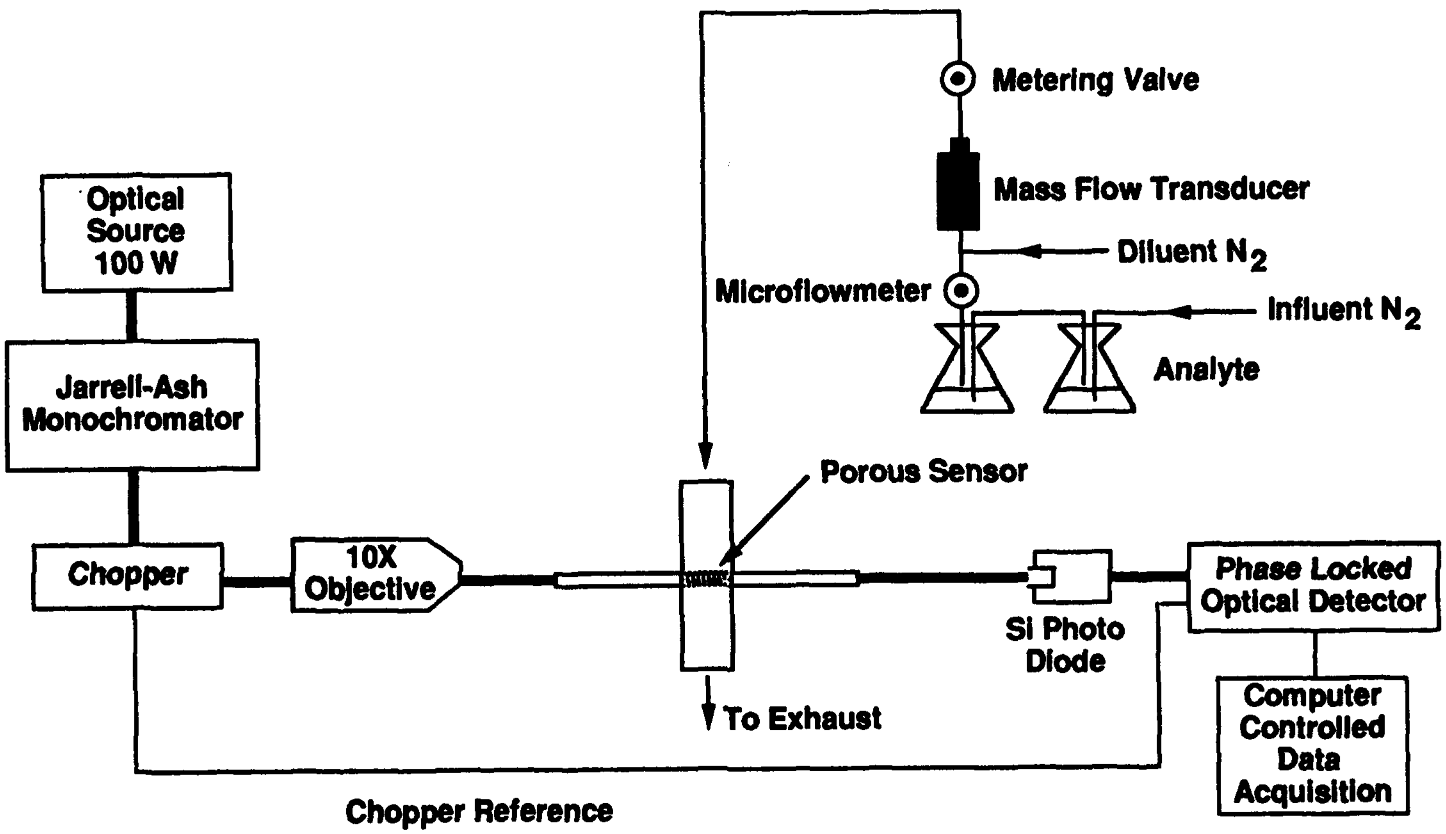


Figure 3. Schematic of Optical System and Test Bed for Phase I Optrode Evaluation

1. Gas Flow System

Referring to Figure 3, a nitrogen (N_2) stream saturated with xylene vapor is obtained by bubbling the inert gas through a multiple stage sparging apparatus. The liquid level of the last stage of the sparge line is monitored for fluid level change. No change ensures a saturated vapor stream. The xylene flow is regulated by either a Gilmont microflowmeter (sub ppm) or Matheson digital mass flow transducer (low ppm) depending on the flow range of interest, and is diluted with additional N_2. All gas flow lines are stainless steel, and after passage through the sensing region the vapor is exhausted to a fume hood. A sample xylene concentration calculation is presented in Appendix A.

A typical experimental run to determine optrode sensitivity and response time involves the following steps:

1. Scan intensity versus wavelength (350-550nm) of untreated porous fiber to check inherent transmission.

2. Impregnate section (~0.5-1cm) of fiber with indicator of known concentration. This is now the sensor, or optrode.

3. Start diluent N_2 flow ($\leq$ 600cm).

4. Realign to optimize transmission, and record intensity versus wavelength from 350-550, and 600-800nm (reference wavelength is ~700nm).

5. Reposition monochromator to desired interrogation wavelength.

6. Open xylene/N_2 sparge line and adjust with fine metering valve to desired flowrate.

7. Record intensity versus time until saturation is reached.

8. Rescan 350-500nm, and 600-800nm (to check reference wavelength).

2. Data Acquisition and Control

There are two primary functions of the data acquisition system: control of the monochromator grating angle (which allows light of known wavelengths and bandwidth to be selected), and detection of the light intensity at that wavelength. An analysis of the initial setup revealed several factors which would affect evaluation of the sensor performance. The quality of the interrogating source is determined by the precision of the wavelength step interval, and accuracy of the wavelength chosen by the grating mechanism. These factors affect evaluation of the sensor spectroscopic characteristics. Detection of the sensor output is limited by the recording rate of the output device.

The accuracy of the interrogating light source, and hence resolution, was not acceptable because of the mechanical limits of the original monochromator grating mechanism. A stepper motor interface provided the finite steps of high accuracy and resolution, as well as repeatability. To access the power of the stepper motor system, a computer controller was incorporated. The Computer Continuum lab 40-5 stepper motor system provided IBM-PC compatibility with simplicity of operation and low cost.

An analysis of the detection components of the sensor system revealed that reading of the analog output of the lock-in amplifier (used to detect the sensor response) would either limit resolution, or compromise the rate of data acquisition. In the case of a rapidly responding sensor operating in real time, the condition was unacceptable. A GPIB data acquisition system with a digital voltmeter (DVM) was incorporated to digitize the analog output of the lock-in, which increased the acquisition rate, thereby, increasing the resolution to 1 part in 65,500.

With these components under computer control, the two systems were functionally integrated. Software was developed to acquire an intensity value at a particular wavelength. The motor then steps a quantified amount to the next wavelength of interest, acquiring another data point until the final wavelength of interest was reached. The result, a plot of light intensity as a function of scanned wavelength, was displayed on the computer as mV versus wavelength. A program was also developed which took the ratio of the spectroscopic curves before and after exposure to the chemical of interest, thereby, revealing details of the absorption feature.

The scanning wavelength program was used to return to the specified interrogation wavelength and the system was poised to measure variations in the intensity with respect to time. A data acquisition rate could be set depending on the sensor response time. The output shows intensity of light in mV versus time. The information contained in this scan shows sample response time and saturation level. The slope of this graph is linearly related to analyte concentration as discussed in Appendix B.

SECTION III

RESULTS

A. SENSITIVITY AND RESPONSE TIME

Optrodes were fabricated and evaluated for sensitivity, response time, reproducibility, and linearity with xylene as the target species. The interrogation wavelength for intensity versus time plots was 470 nm, which is near the peak absorption for the TCNE:xylene adduct formed. There is increased absorption in the blue (which corresponds to decreasing transmission intensity) as the xylene reacts with the TCNE. Summaries of the intensity versus time curves are presented in Figures 4-6. These data are representative of a minimum of two (and often more) experimental runs. The excellent sensitivity of the optrodes (~40ppb) with near real time response (<1 minute) is note worthy. The actual intensity changes are 2-3 orders of magnitude.

Experiments were performed with three different TCNE concentrations: 10 mg/ml, 5 mg/ml and .5 mg/ml. As shown in Figure 7 the sensitivity increases at higher indicator concentrations; that is, for any given time interval the change in optical intensity is greater at higher indicator concentrations. The TCNE is dissolved in dichloromethane (DCM), and the response of a TCNE treated fiber (i.e., the sensor) to additional application of DCM is shown in Figure 8. The DCM readily drys at room temperature with no change in original sensor transmission (i.e., no reaction of the TCNE with DCM).

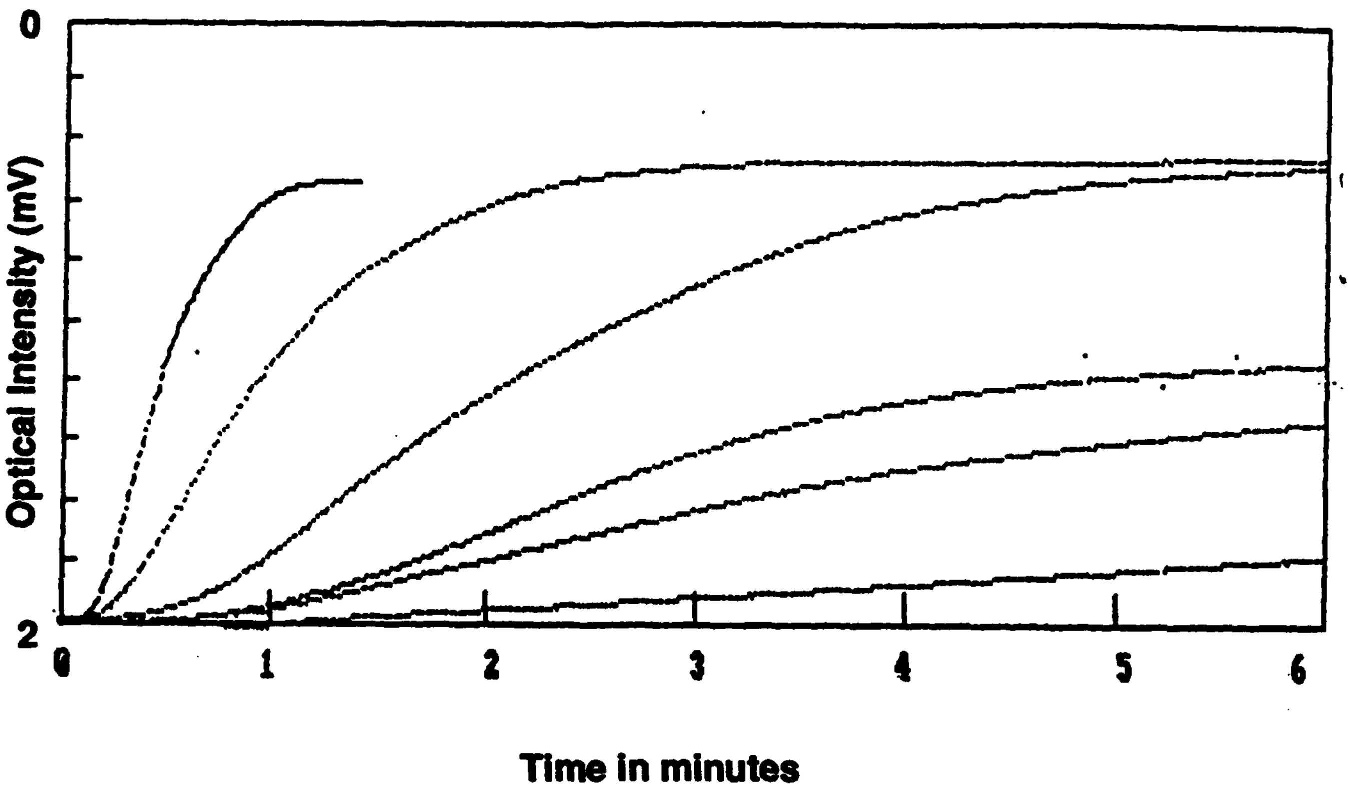


Figure 4. Response Curves for Porous Glass Xylene Sensor at 470nm and 5 mg/ml TCNE. Xylene Concentrations Range from 2ppm to ~40ppb.

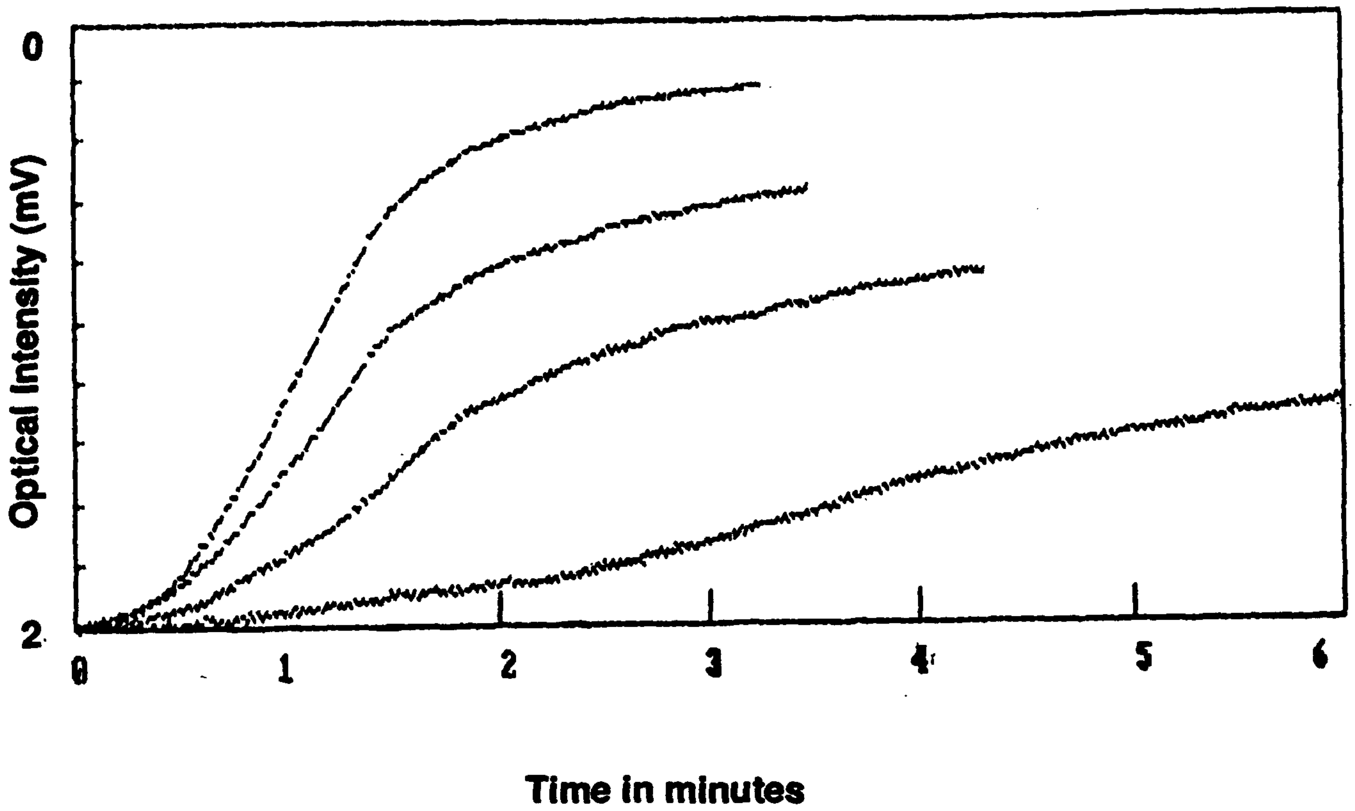


Figure 5. Response Curves for Porous Glass Xylene Sensor at 470nm and 0.5 mg/ml TCNE. Xylene Concentrations Range from 320ppb to <40ppb.

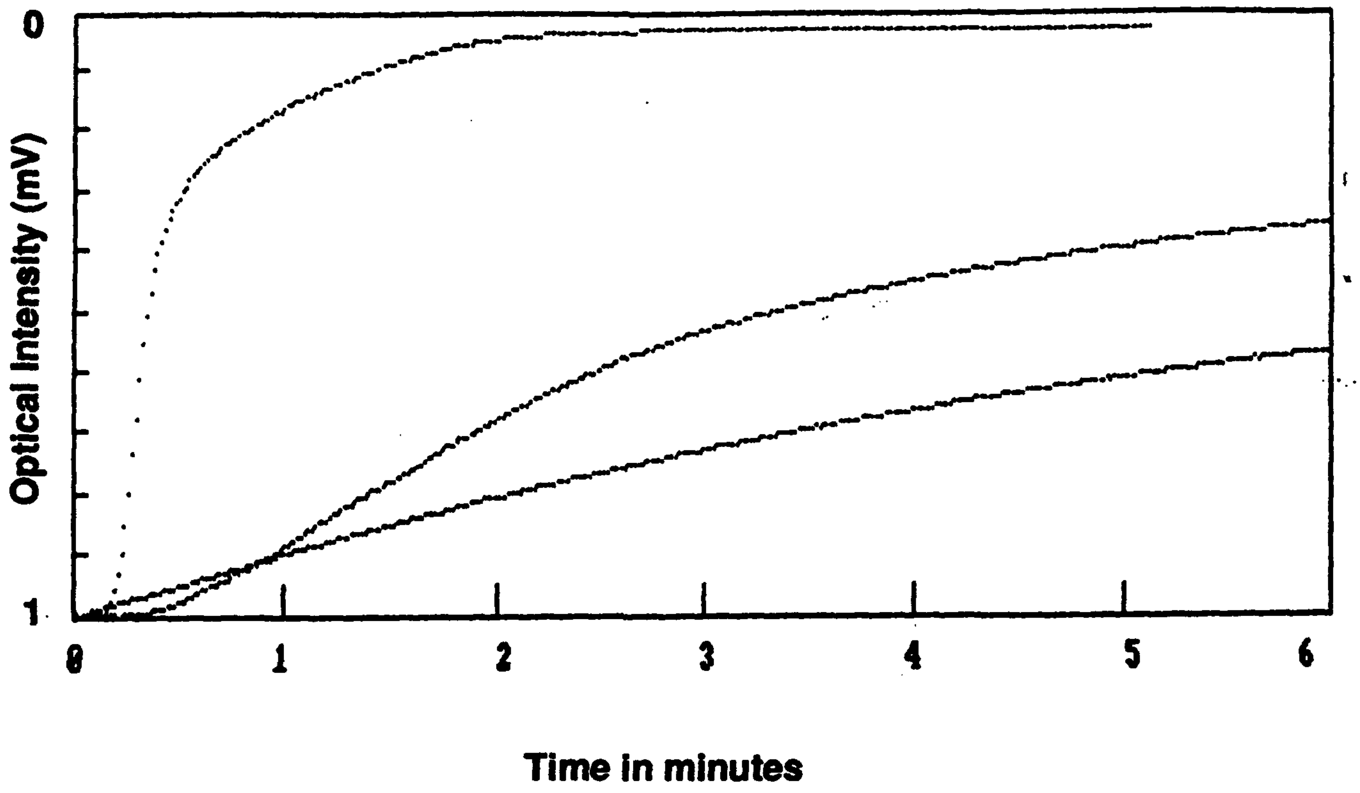


Figure 6. Response Curves for Porous Glass Xylene Sensor at 470nm and 10 mg/ml TCNE. Xylene Concentrations Range from 1ppm to ~40ppb.

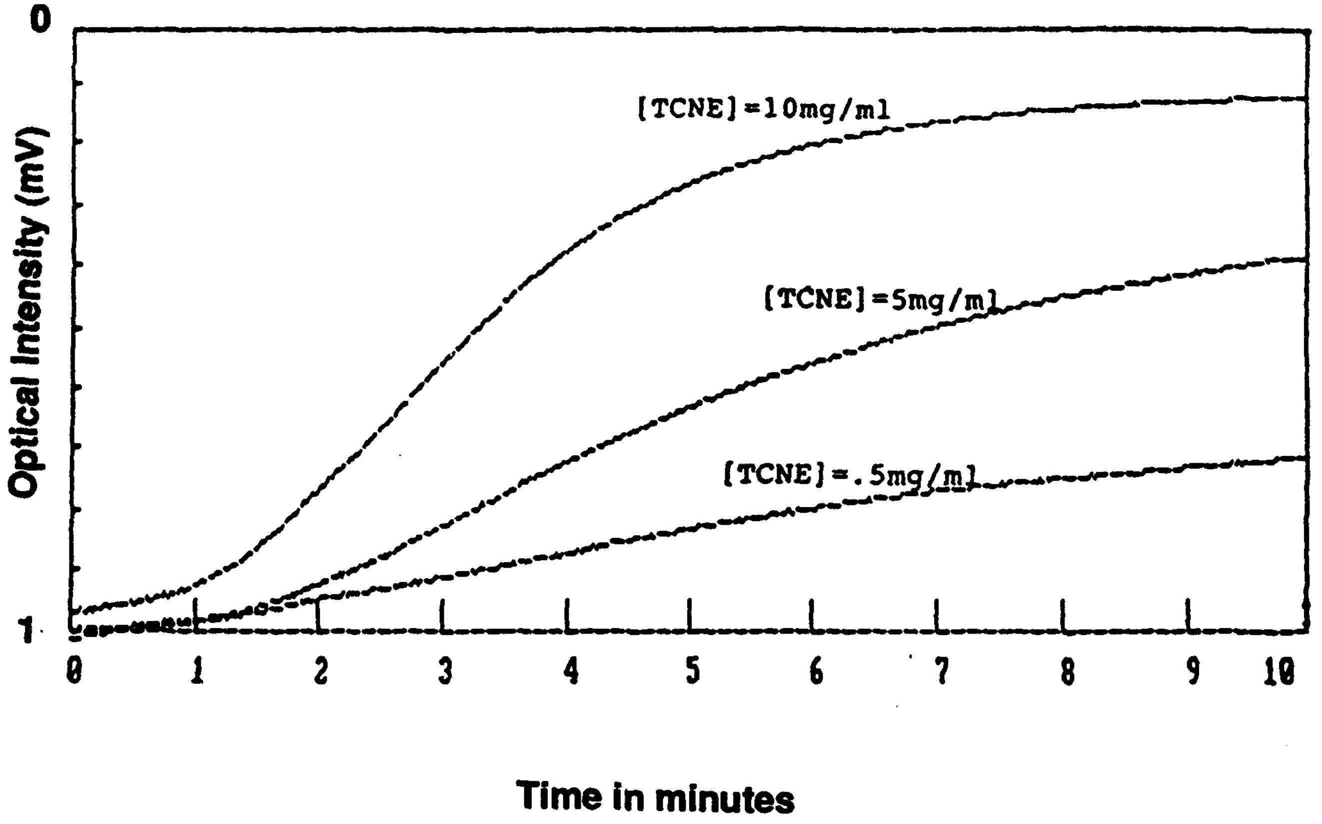


Figure 7. Response Curves for a Porous Glass Xylene Sensor as a Function of Indicator Concentration. [Xylene] = 430ppb.

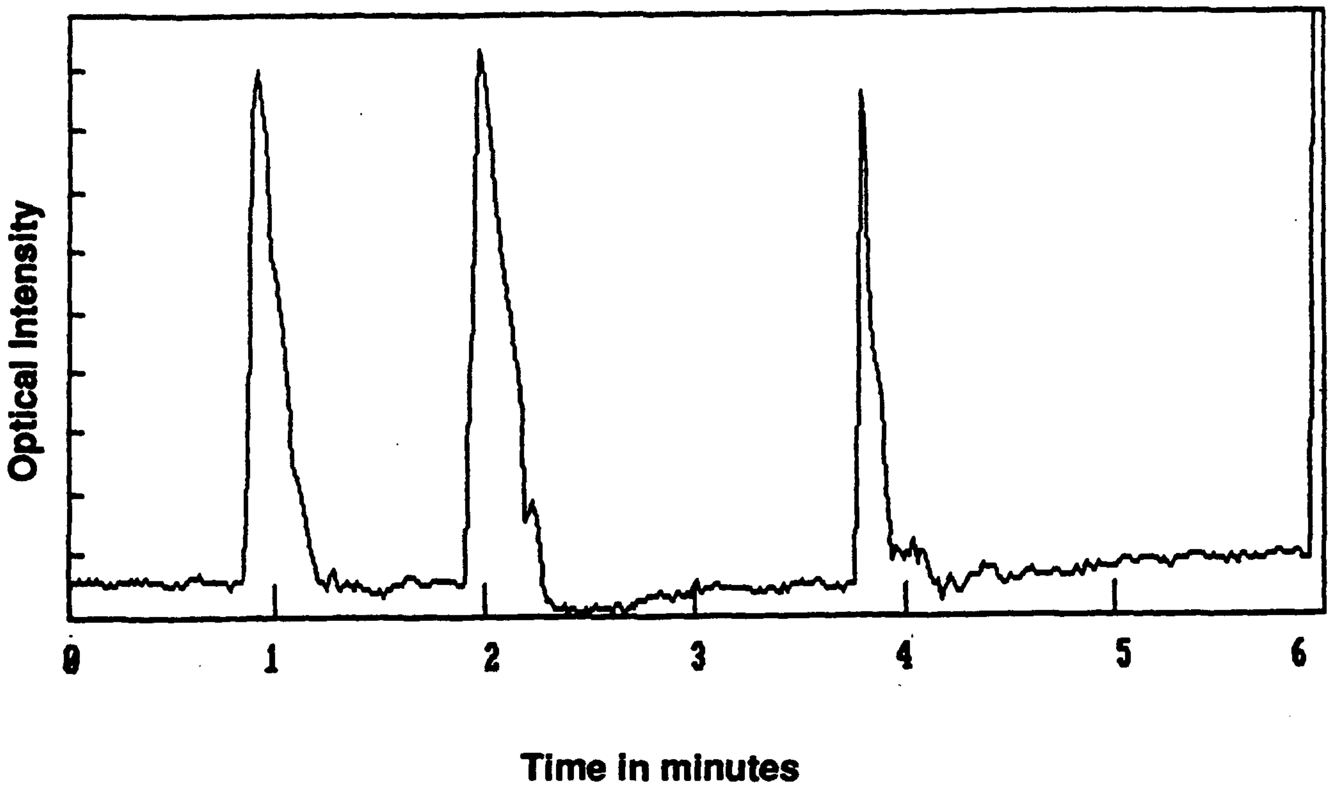


Figure 8. Time Scan at 470nm Showing the Sensor Response to Repeated Exposure to Dichloromethane. This indicates that there Is no TCNE : solvent complex formed.

B. LINEARITY AND REPRODUCIBILITY

The TCNE reacts irreversibly with xylene to form a transient adduct under our experimental conditions. This implies that the reaction proceeds to saturation (i.e., when all the TCNE is consumed), rather than reaching some point of chemical equilibrium. Details of the kinetics are presented in Appendix B, and indicate that the slope of the intensity versus time plots are proportional to concentration. The plots of slope versus concentration are shown in Figures 9-11, and demonstrate good sensor linearity from the low parts per billion to low parts per million.

The slopes calculated from the intensity versus time curves show a reproducibility of ~5 percent, and are representative of a minimum of two experimental runs, and often more.

C. SELECTIVITY

In Phase I concept feasibility was demonstrated using o-xylene as the target aromatic hydrocarbon. Groundwater monitoring requires the measurement of the aromatic content known as BTEX (benzene, toluene, ethylbenzene and o-xylene). The quantification of benzene is of particular interest due to its carcinogenicity. Absorption curves for the optrode response to benzene, toluene and xylene are shown in Figure 12. The absorption peaks for the TCNE:Ar-HC adduct are separated by approximately 30 nm suggesting that individual aromatic components may be quantified. The use of multi-wavelength techniques will be addressed in Phase II.

Non-aromatic hydrocarbons comprise approximately 80 percent of jet fuels. The indicator system developed in Phase I was bench tested for responsivity to the saturated alkanes, octane, heptane

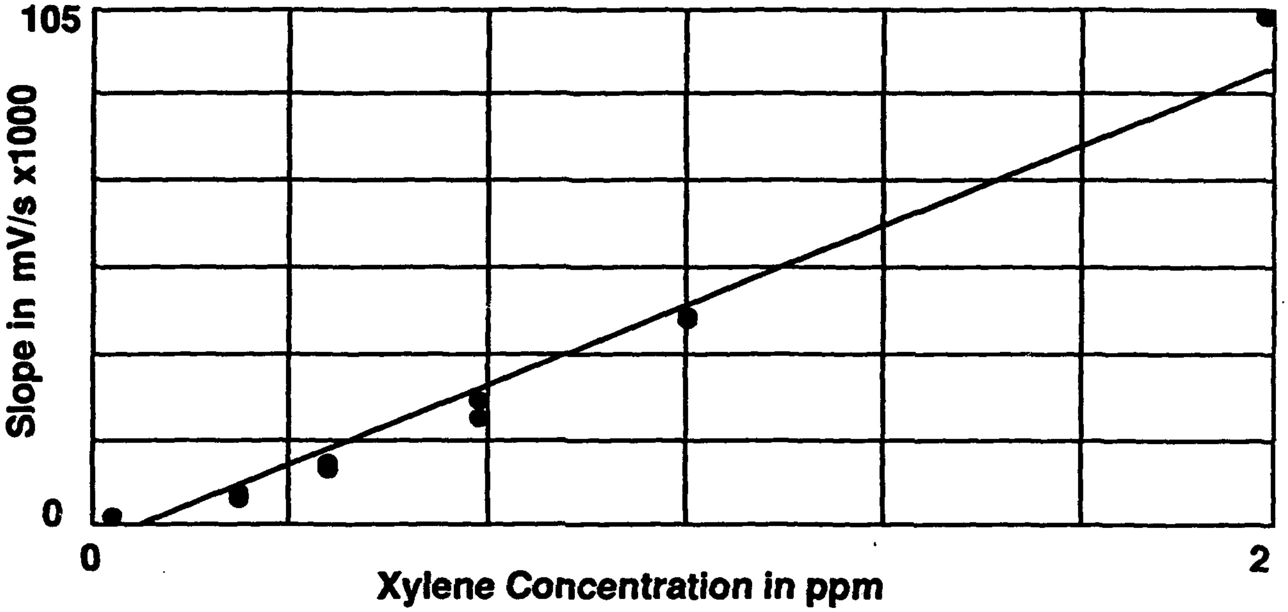


Figure 9. Calibration Curve for Xylene Optrode Based on Porous Glass Fiber. [TCNE]=5mg/ml.

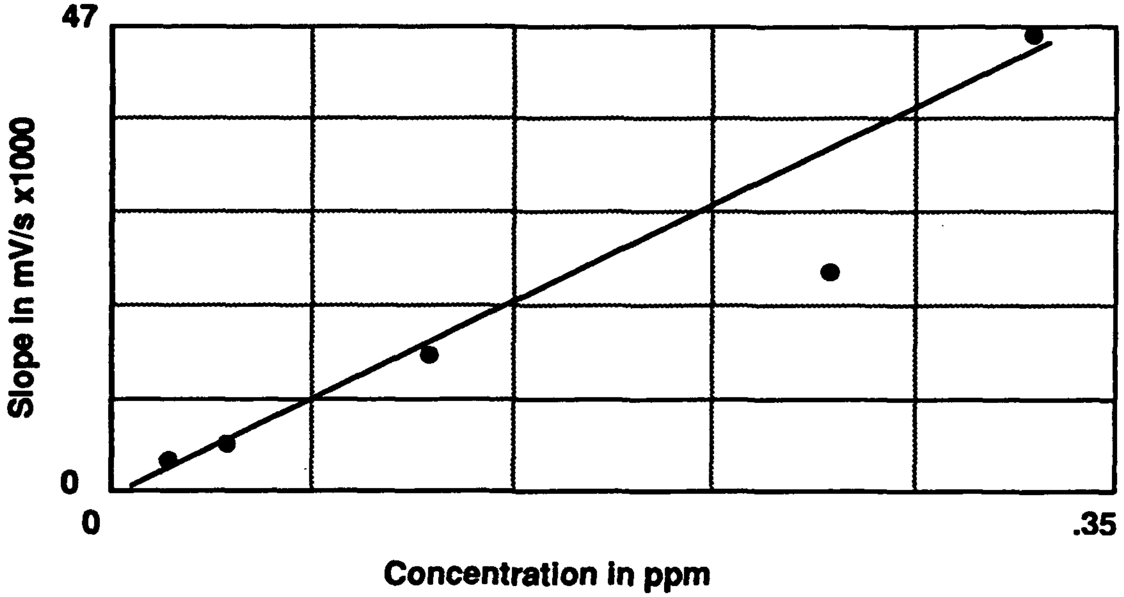


Figure 10. Calibration Curve for Xylene Optrode Based on Porous Glass Fiber. [TCNE] = .5 mg/ml.

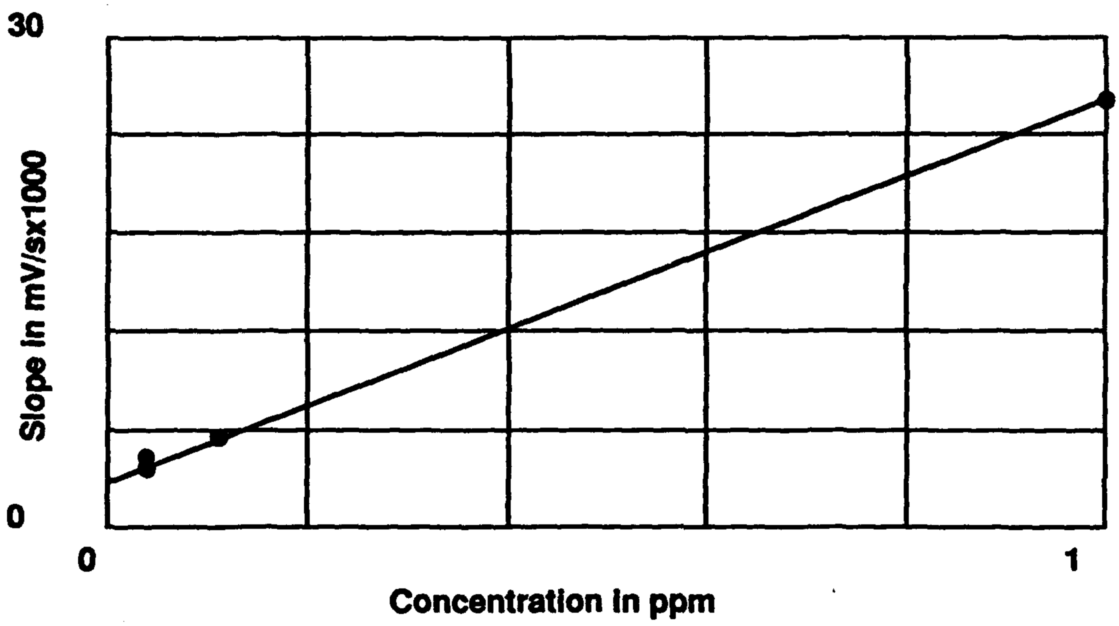


Figure 11. Calibration Curve for Xylene Optrode Based on Porous Glass Fiber. [TCNE]= 10 mg/ml.

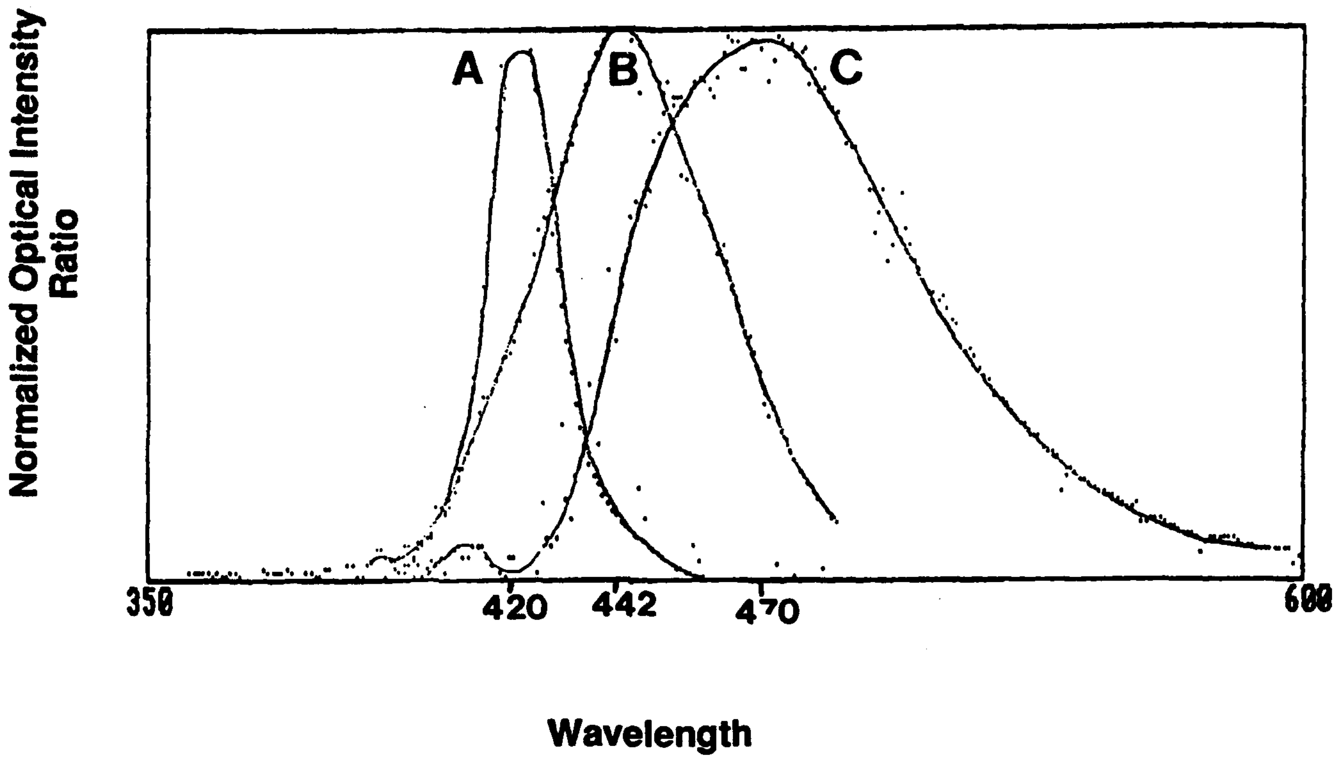


Figure 12. Aromatic Hydrocarbon Optrode Response to Benzene, Toluene and Xylene Respectively. A:benzene B:toluene C:xylene

and a cyclic alkane. As shown in Figure 13 the sensor is inert to these interferents. The ratio of sensor transmission before and after exposure to octane shows no change in the 350-500 nm region, and therefore, no response. Preliminary studies were performed toward the end of the effort to determine the effects of water vapor. These were inconclusive.

D. REVERSIBILITY

As discussed in the subsection on "linearity" and in Appendix B the indicator/analyte system chosen in Phase I is not reversible. However, we have observed fiber recovery with time after exposure to the aromatic analyte. This result is consistent with the formation of a transient adduct, Reference 9. Figure 14 demonstrates fiber recovery with time. Simple treatment with solvent may well restore fiber transmission completely, leaving it ready for subsequent treatment with the indicator. This, coupled with the rapid drying of the DCM solvent (Figure 8) suggests minimum down time and manning requirements for the sensor as currently configured.

It would be advantageous to find a reversible indicator system for a sensor probe and essential for any long-term distributed sensor network. The TCNE system may be reversible under certain circumstances, but the search for, and development of, a new (although perhaps chemically related) indicator system should be a primary thrust of the early months of a Phase II effort.

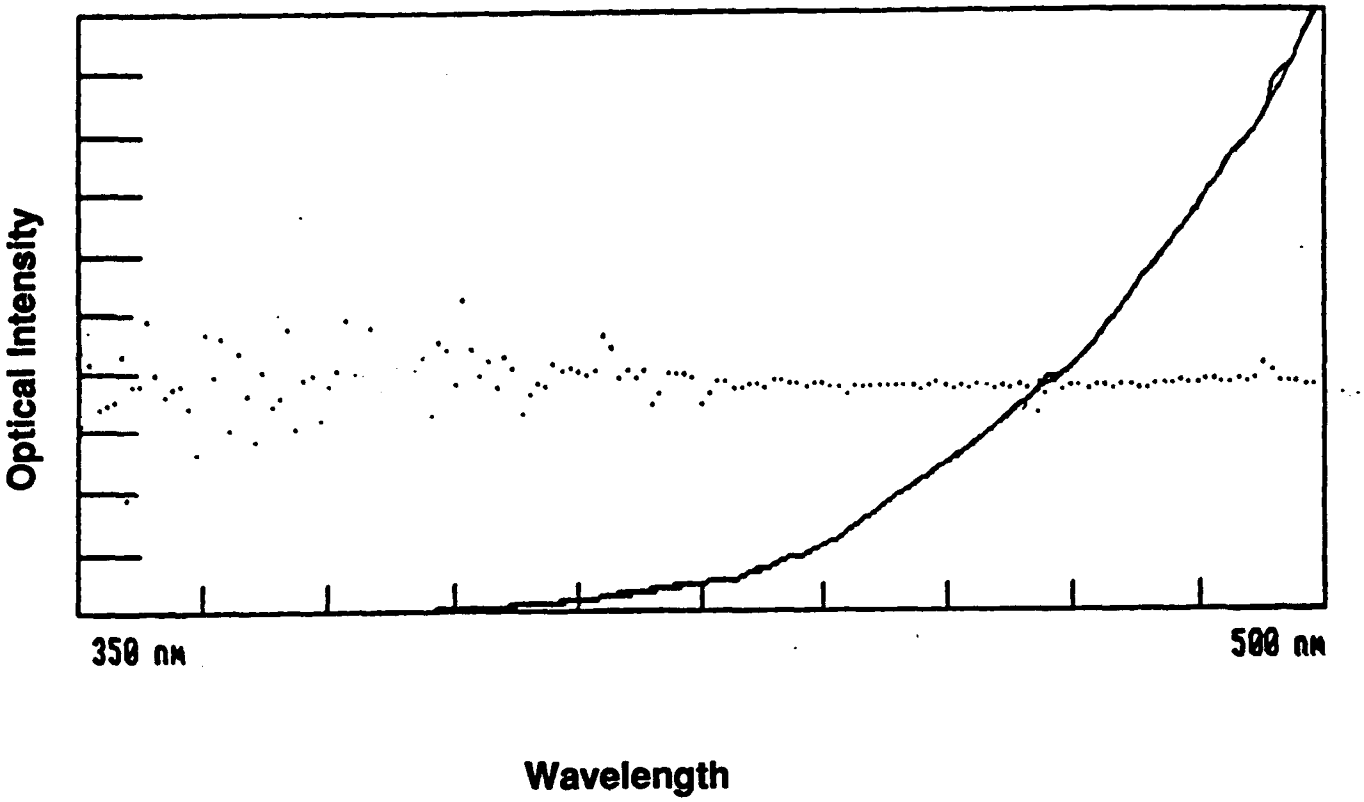


Figure 13. Transmission as a Function of Wavelength for a Porous Glass Sensor Before and After Exposure to Octane. Note the data points in the center, which are a ratio of the before and after traces, indicating that the sensor is inert to saturated hydrocarbon fuel constituents.

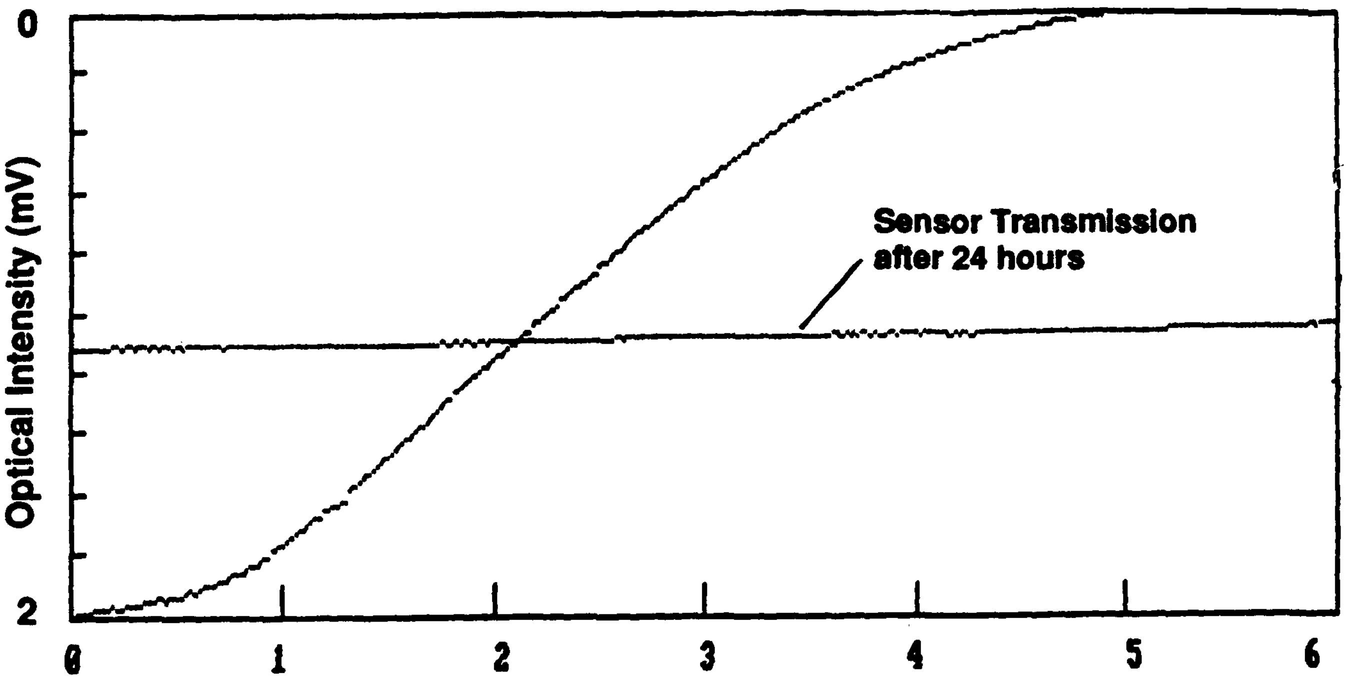


Figure 14. Response Curve of Sensor to 0.4 ppm Xylene, and Sensor Recovery.

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

In the Phase I program, porous fiber sensors for detection of aromatic fuel constituent vapors was designed, fabricated and evaluated. Optrodes was characterized for the target species, xylene and excellent sensitivity to <50ppb demonstrated. Response time, reproducibility, linearity, selectivity, and reversibility was also determined or addressed. Optrode selectivity for benzene and toluene was also demonstrated. These laboratory results indicated that highly sensitive optrodes, with near real time response and the capacity for selective detection of target species were feasible.

Having successfully met the program technical objectives, a Phase II advanced research and development effort with the following objectives is recommended.

1. Improve device characteristics, especially sensitivity and selectivity, of the vapor optrode designed in Phase I.

2. Identify alternative indicator/analyte systems with emphasis on reversibility, specificity and stability.

3. Design and evaluate sensors specifically for groundwater monitoring based on complementary adaptations of the technology demonstrated in Phase I, (e.g., chemical immobilization on porous glass, use of porous polymer fibers).

4. Evaluate the most promising prototype optrode under the environmental conditions prevalent in a typical groundwater monitoring application. Sensitivity to total BTEX, and selectivity in the presence of interferents will be determined.

5. Design and evaluate optrodes for other target species of interest such as chlorinated hydrocarbons, solvents and CO_2.

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APPENDIX A

CALCULATIONS FOR ANALYTE CONCENTRATIONS (C_{FEED})

The partial pressure of xylene at room temperature (25°C):

6.55 torr

Using the ideal gas law to convert torr to moles/l we get:

$6.55 \text{ torr} = 3.54 \times 10^{-4} \text{ moles/l}$

Using an exemplary sparge flow rate we get a sparge concentration (C_{SPARGE}) of:

$C_{SPARGE} = \text{moles/l} * .0053 \text{ l/min}$

OR

$C_{SPARGE} = 1.87 \times 10^{-6} \text{ moles/min}$

Using the total flow rate we get a feed concentration (C_{FEED}) of:

$C_{FEED} = \text{moles/min} \div .6 \text{ l/min}$

OR

$C_{FEED} = 3.11 \times 10^{-6} \text{ moles/l}$

Multiplying by the molecular weight of xylene:

$C_{FEED} = \text{moles/l} * 106.17 \text{ g/mole}$

$= 3.3 \times 10^{-4} \text{ g/l}$

Convert to ppb by dividing by the density:

$C_{FEED} = \text{g/l} \div .8802 \text{ g/ml} \div 1000 \text{ ml/l}$

$C_{FEED} \doteq 375 \text{ ppb.}$

APPENDIX B

KINETIC MODEL FOR TCNE:XYLENE REACTION

Assuming the reaction is nonreversible and diffusion is the kinetic controlling step:

$$R = A\ D\ C_{xy} \tag{1}$$

where R is the reaction rate of TCNE (dC_{add}/dt), A is a constant related to fiber properties, D is the xylene diffusion coefficient in the porous fiber, and C_{xy} is the concentration of xylene outside the fiber.

The light intensity is a function of the concentration of the TCNE:xylene adduct (C_{add}):

$$I = I_o \mathrm{Exp}\ (-h\ C_{add}) \tag{2}$$

where I_o is the intensity of the incident light, h is the extinction coefficient (light absorption and light scattering by the adduct).

Initially the adduct concentration is very small and equation 2 can, therefore, be written as:

$$I = I_o\ (1-h\ C_{add}) \tag{3}$$

Taking the derivative of Equation 3, and substituting Equation 1 into the result

$$\frac{dI}{dt} = -I_o h\ A\ D\ C_{xy} \tag{4}$$

Equation 4 suggests that the light intensity should show a linear decrease with time upon exposure to xylene, and that the slope of the decay curves (dI/dt) should be linearly proportional to the xylene concentration.

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