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OCA PAD AMENDMENT - PROJECT HEADER INFORMATION

08/18/94

Active

Project #: E-20-X13
Center #: 10/24-6-R7535-0A0

Cost share #: E-20-354
Center shr #: 10/22-1-F7535-0A0

Rev #: 12
OCA file #:
Work type : RES
Document : SUBCONT
Contract entity: GTRC

Contract#: RP160708
Prime #: R819165-01-0

Mod #: 5

Subprojects ? : Y
Main project #:

CFDA: N/A
PE #: N/A

Project unit:
Project director(s):
SAUNDERS F M
WALSH J L JR
HUGHES K D

CIVIL ENGR
CIVIL ENGR
EOEML
CHEMISTRY

Unit code: 02.010.116
(404)894-2265
(404)-

Sponsor/division names: LSU
Sponsor/division codes: 400

/ BATON ROUGE, LA
/ 131

Award period: 920201 to 940930 (performance) 941130 (reports)

Sponsor amount	New this change	Total to date
Contract value	35,000.00	172,100.00
Funded	35,000.00	172,100.00
Cost sharing amount		34,275.00

Does subcontracting plan apply ? : N

Title: DEVELOPMENT OF AN INTEGRATED-OPTIC INTERFEROMETER FOR IN-SITU MONITORING OF..

PROJECT ADMINISTRATION DATA

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894-4820

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Security class (U,C,S,TS) : U

ONR resident rep. is ACO (Y/N): N

Defense priority rating : N/A

N/A supplemental sheet

Equipment title vests with: Sponsor X
NONE PROPOSED.

GIT

Administrative comments -

AMENDMENT #5 AUTHORIZES INCREMENTAL FUNDS OF \$35,000 (TO BE CREDITED TO
"SUB-PROJECT" A-9416/WALSH/EOEML).

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 12/04/95

Project No. E-20-X13

Center No. 10/24-6-R7535-0A0

Project Director SAUNDERS F M

School/Lab CIVIL ENGR

Sponsor LSU/BATON ROUGE, LA

Contract/Grant No. RP160708 Contract Entity GTRC

Prime Contract No. R819165-01-0

Title DEVELOPMENT OF AN INTEGRATED-OPTIC INTERFEROMETER FOR IN-SITU MONITORING

Effective Completion Date 950930 (Performance) 951130 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	
Final Report of Inventions and/or Subcontracts	Y	
Government Property Inventory & Related Certificate	N	
Classified Material Certificate	N	
Release and Assignment	N	
Other	N	
Comments		

Subproject Under Main Project No.

Continues Project No.

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Management	Y
Research Security Services	N
Reports Coordinator (OCA)	N
GTRC	Y
Project File	Y
Other	N

NOTE: Final Patent Questionnaire sent to PDPI.

Semi-Annual Progress Report

August 2, 1993

Title of Project: Development of an Integrated-Optics Interferometer for In-Situ Monitoring of Volatile Hydrocarbons

Principal Investigators: James L. Walsh, Nile F. Hartman, Charles C. Ross, Kenneth D. Hughes, David M. Collard

Initiation Date of Study: February 2, 1992
Scheduled Completion: November 30, 1994

Period Covered by Report: (February 1, 1993 - July 31, 1993)

Objectives of Study: Design and development a sensor(s) capable of measuring the concentrations of benzene, toluene, ethyl benzene, and xylene (BTEX) in soil vapors. The sensor will be based on the integrated-optics (IO) technology patented by Georgia Tech. The major tasks involved in the process are the selection of a surface coating for the IO sensor that will react with the chemical being detected, testing of the coatings under controlled conditions, and design and testing of an integrated sensor package for field testing. The field testing may be conducted with the cone penetrometer currently being developed by the U. S. Army. The sensor has the potential for evaluation of contaminated sites as well as detection of leaks for underground gasoline tanks.

Progress During Reporting Period:

The major work since January 1, 1993 has been the screening of waveguide coating materials to determine the sensitivity to benzene, toluene, ethyl benzene, and xylene, the BTEX chemicals found in gasoline leaks. As reported at the February meeting, polyvinyl alcohol (PVA) has a positive response to water vapor and all BTEX chemicals except ethyl benzene. The PVA showed strong sensitivity to water vapor which indicates the chemical could be used for nulling the effects of water.

The other chemicals tested include polydimethylsiloxane (PDMS), poly (isodecyl) methacrylate, and polyurethane. These chemicals were also tested with water vapor and all the BTEX chemicals except ethyl benzene. A number of other coating materials are planned for evaluation. The objective is to develop a matrix indicating the response of each coating to the BTEX chemicals and water vapor. The matrix will determine the coatings to be used for the actual sensor design.

Georgia Tech

RESEARCH INSTITUTE

E-20-X13
2,3,4,5

Georgia Tech Research Institute
Georgia Institute of Technology
Atlanta, Georgia 30332-0800
USA

August 23, 1994

Hazardous Substance Research Center/South & Southeast
3418 CEBA Building
Louisiana State University
Baton Rouge, LA 70803

Enclosed are the Quality Assurance and Quality Control and Safety Plan and Progress Report for the project Development of an Integrated Optics Interferometer for In-Situ Monitoring of Volatile Hydrocarbons

Sincerely,

James L. Walsh
Co-Project Director

QUALITY ASSURANCE/QUALITY CONTROL AND SAFETY PLAN

For Project

**Development of an Integrated Optics Interferometer
for In-Situ Monitoring of Volatile Hydrocarbons**

Submitted to

**Hazardous Substance Research Center/South & Southeast
3418 CEBA Building
Louisiana State University
Baton Rouge, LA 70803**

Submitted by

**James L. Walsh, Jr., P.E.
Senior Research Engineer
Georgia Tech Research Institute
Georgia Institute of Technology
039 O'Keefe Building
Atlanta, GA 30332**

August 22, 1994

PROJECT DESCRIPTION

The underground storage tank (UST) provisions of the Resource Conservation and Recovery Act mandate that all USTs have leak detection by December 22, 1993. Several of the methods acceptable to the U. S. Environmental Protection Agency (EPA) involve the use of sensors for detecting leaks in soil or water. One technique for accomplishing this detection measurement for gasoline storage tanks is to sense the presence of the BTEX chemicals (benzene, toluene, ethyl benzene, and xylene). In addition, these four chemicals have been found at a large number of Superfund sites and are suspected to exist at even more. New site investigations systems such as the cone penetrometer are being developed which could make use of microsensor technology.

There are existing techniques for measuring these substances, but these are often prohibitively expensive, time consuming, and sometimes difficult to use in the field. There have been some advances in microsensors, such as fiber optic chemical sensors (FOCS), for detecting these chemicals. However, these techniques have been limited by problems with repeatability in manufacturing, operation longevity, shelf life, and the capability for only single species differentiation and have external chemical (fluorescence) requirements.

Georgia Tech has developed and patented an integrated optic (IO), interferometric chemical sensor capable of continuously measuring an individual chemical species in the ppb range. This technology offers the potential of monitoring several different chemical species on a single, multichannel waveguide in a package no larger than a cigarette. Moreover, the device can be designed to negate many of the effects associated with a soil/water environment such as moisture changes, temperature variations, and chemical contamination.

The three-phased effort proposed herein is intended to develop a multi-channel, (IO) interferometer for the continuous monitoring of the BTEX chemicals. The goal for the first year of research will be to develop a sensor for measurement of benzene (and possibly xylene) with the addition of the other chemicals in subsequent years. The sensor system will be developed for application in monitoring both gas and liquid phases such that several of the EPA release monitoring requirements can be met. The device offers to be a significant improvement to recent FOCS designs and has the potential to offer a lower cost (estimated at \$150), more usable alternative to current monitoring techniques.

PROJECT ORGANIZATION AND RESPONSIBILITY

The co-project directors will be James L. Walsh, Jr. and Nile F. Hartman of the Georgia Tech Research Institute. Mr. Walsh will be responsible for integration of the sensor with the proposed environmental applications including monitoring of underground storage tanks and field analyses using devices such as cone penetrometers. Mr. Walsh will have the primary responsibility for the implementation of the safety aspects of the program. Mr. Hartman will be responsible for development of the sensor system including the integration of the optical and surface chemistry technologies, bench scale development testing, and design of the final field test sensor system. Mr. Hartman will also be primarily responsible for the implementation of the quality assurance and quality

control aspects of the program. The principal investigators will include Messrs. Walsh and Hartman and Drs. Kenneth D. Hughes and David M. Collard of the School of Chemistry and Biochemistry at the Georgia Institute of Technology, and their primary responsibility will be the selection of surface coatings. Additional project personnel will include Drs. Daniel P. Campbell and Dr. Robert E. Schwerzel who will also be involved in the selection of surface coatings. The laboratory testing will be conducted by a graduate student, Mr. Umesh Akki.

DATA QUALITY OBJECTIVES

The data quality objectives are to measure in-situ the concentrations of benzene, toluene, ethyl benzene, and xylene (BTEX) in the part per billion (PPB) range with an accuracy of less than 1%. These in-situ measurements will detect the BTEX chemicals in soils by sensing soil gases and detect the same chemicals in sediments by sensing the chemicals in the aqueous phase.

SAMPLING PROCEDURES

The development program will require that three types of samples be used. The first part of the program will use gaseous samples of the BTEX chemicals that are obtained from standard laboratory supply companies. These samples will be diluted in a double-dilution gas mixing system to the required concentration for the test and blown over the surface of the waveguide.

The second part of the program will require the mixing of pre-determined amounts of the BTEX chemicals in containers filled with soil or sediment. These chemicals will also be obtained from standard laboratory supply companies. The sensor will be inserted into the sample for measurement of the concentration of the chemical in the container.

The third part of the program will test the sensor at an actual contaminated site. The concentration of the BTEX chemical(s) at the site will be determined from existing data for the site, but sample checks will also be made on a random basis.

ANALYTICAL PROCEDURES

A number of different analytical procedures will be used during the development program. The first two parts of the testing program will use chemicals purchased from standard laboratory supply companies. It is assumed that these chemicals will meet the purity specified by the supplier; but periodic checks using a gas chromatograph will be made to assure quality. The diluted sample used during the first phase of testing also be periodically analyzed using gas chromatography to verify the calibration of the double-dilution gas mixing system. Samples of pre-contaminated soil or sediment and the random samples from an actual site will also be periodically checked using solvent extraction and gas chromatography.

DATA REDUCTION, VALIDATION, AND REPORTING

Data generated from the sensor and gas mixing system are recorded by computer and sensor calibration curves are generated. Multiple tests are conducted for each contaminant concentration and linear regression is used to compute the calibration curves. In addition, tests are conducted at for the same contaminant on different days to determine any effects from degradation of surface coating, surface masks, and other sensor components that may be affected by time.

Since the objective of the program is to develop a single sensor that can detect all four BTEX chemicals using a single waveguide, tests will be conducted with two, three, and all four chemicals using a variation of the concentration of the chemicals. The objective will be to determine any interference problems. The potential interference of water will also be evaluated since this chemical will likely be present in soil gases and will be present in sediment.

All data collected will be presented in semi-annual, annual, and final reports.

SAFETY

The project will be conducted in accordance with the Georgia Tech General Laboratory Manual, Fire and Life Safety Manual, and the Health and Safety requirements in Section 9.0 of the Georgia Tech Office of Human Resources Policies and Procedures.

STATUS REPORT

DEVELOPMENT OF AN INTEGRATED OPTIC INTERFEROMETER FOR IN-SITU MONITORING OF VOLATILE HYDROCARBONS

James Walsh
Nile F. Hartman
Electro-Optics, Environmental and Materials Lab
GTRI

INTRODUCTION

This program is focused on the development of an integrated optic (IO) microsensor suitable for detection and continuous monitoring of BETX chemical species (benzene, ethyl benzene, toluene and xylene) trapped at low concentration levels in river or lake bed sediment layers. The sensor has proven to be capable of detecting contaminant species of interest in both the vapor and aqueous phase, resulting in an ability to perform sensing functions in sediment layers, soil, water or air. This feature ensures several of the EPA release monitoring requirements can be met. Because the device is potentially very low cost, it is expected to provide an attractive alternative for hazardous site monitoring and characterization. With minor modifications, the sensor may also be used to monitor other contaminant species such as metal ions.

Early program activities focused on screening and selection of candidate coatings for benzene and toluene and characterizing device responsivity. The most recent activities have focused on packaging and protective mechanisms to withstand the harsh conditions expected to be encountered in actual applications. Permeable membranes and fluorinated surfaces have been tested and found to be suitable for protective purposes.

TECHNICAL DISCUSSION

The microsensor is based on an integrated optic (IO) interferometer that is capable of detecting extremely small refractive index changes ($\leq 10^{-6}$) at the surface of the IO waveguide. By coating the waveguide with a thin film that exhibits a response in the presence of low levels of a chemical species, a highly sensitive chemical detector results. In the case of BETX chemicals, selected polymers are applied to the waveguide surface and these polymers tend to swell or exhibit a refractive index change due to solvent infiltration. Detection of benzene and toluene has been demonstrated at the low part-per-million by volume (ppmv) range using a laboratory device.

Experimental Results

A variety of polymeric materials were screened and evaluated for sensing purposes. Selection criteria included a) responsivity to benzene, toluene, and xylene, b) susceptibility to water vapor in the case of gaseous phase sensing, c) optical properties of the coatings, and d)

physical properties (hardness, water solubility and etc.). Two promising coating have been evaluated, these being poly(isodecyl methacrylate) and a urethane. The response of a silicon nitride/fused silica waveguide/substrate system using these coatings has shown benzene and toluene concentration levels are easily detected at the 1 to 2 ppmv level. Poly(isodecyl methacrylate) is particularly promising for vapor phase measurements as it shows little or no response to water vapor. The time dependent response of this sensing combination is quite fast, with less than 0.1 seconds being typical.

Waveguide Protection The proposed use of the sensors includes monitoring BETX chemicals in river bed and lake bottom sediments. Some protection for the waveguide surface is required in this environment and two approaches are being pursued. The first relies on fluorinating or silanating the surface of the waveguide to provide a low energy surface which tends to limit the sticking of fine sedimentary materials to the waveguide surface. The fluorination step is performed by exposing the polymer coated waveguide to a fluorinated gas in a low pressure plasma. This has been done without degrading the sensing function. Secondly a vapor or aqueous phase permeable membrane has been used to shield the waveguide surface from the sedimentary muck. Two modes of operation were evaluated, wherein, 1) the membrane only allows vapor phase transport of the volatile hydrocarbons while water and sedimentary particles are shielded from the waveguide surface and 2) the membrane allows water to transport through the membrane while blocking sediments. The protective membrane was secured through an arrangement with W. L. Gore & Associates, Inc.

Actual *in-situ* characterization of the protective properties of the "Gore" encapsulated and fluorinated waveguides was performed with the aid of the Environmental Division of ISCO, Inc. ISCO personnel placed test devices in various sewer system sites where the samples were allowed to set in the sewer sediment for a three week period. The samples were then retrieved and evaluated by visually examining the waveguide surface and characterizing the waveguide performance. The Gore membranes used for this test were designed to transport water and block sedimentary residue and in this regard performed very well. The samples retrieved typically were coated with a thick layer of "crud" on the exterior of the package while the interior remained clean. No apparent damage to the waveguide surface was observed with one exception. One particular test site was characterized by high pH levels that were routinely in the 9.5 to 10 range and at times exceeded 11.0 at temperatures up to 65 °C. Waveguides exposed to these conditions for a three week period exhibited some evidence of etching of the glass substrate and damage to the waveguide surface. Furthermore the silanated films were partially removed by the high pH conditions. In general the proposed application is expected to be much more benign than the environment encountered in the sewer settings and the protective schemes should function well.

Packaging The proposed package will use a fiber optic delivery and collection system. This will permit the source and detector electronics to be remotely located with respect to the sensor measurement site. Grating couplers will be used to couple light into and out of the waveguide sensor. Test grating couplers have been fabricated and successfully demonstrated.

FUTURE PLANS

The activities to develop a sensor package for sediment applications will continue.

Simultaneously more advanced test of protected waveguide sensor configurations and sensor performance in simulated conditions will be undertaken. Concurrently, new sensing layers will be continually evaluated and/or developed.

Georgia Tech

RESEARCH INSTITUTE

E-20-X13

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Atlanta, Georgia 30332-0800
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March 29, 1995

Hazardous Substance Research Center/South & Southeast
3418 CEBA Building
Louisiana State University
Baton Rouge, LA 70803

Enclosed is the semi-annual Progress Report for the project Development of an Integrated Optics Interferometer for In-Situ Monitoring of Volatile Hydrocarbons for the period of August 1, 1994 to January 31, 1995.

Sincerely,

James L. Walsh
Co-Project Director

Semi-Annual Report

Integrated Optic Sensor For Detection of Volatile Hydrocarbons

by

**James Walsh
Nile Hartman**

to

**Hazardous Substance Research Center
Louisiana State University
Baton Rouge, Louisiana**

This report covers the period of August 1, 1994 through January 31, 1995. The object of this program is the development and demonstration of an integrated optic sensor for the detection of BTEX chemicals trapped in sediment layers.

Sensor Description

The basic sensor relies on an integrated optic interferometric sensor. Chemical selectivity is achieved by coating the surface of the waveguide with a thin film designed to be interactive with the species of interest. For this application polymeric sensing layers have been selected that have shown good sensitivity to benzene and toluene in the low ppmv range. The design and fabrication of a packaged two channel sensor suitable for preliminary testing in sediment layers has been the focus of the activities during this reporting period.

Sensor Configuration and Protective Package

In addition to the waveguide sensing element, the sensor package includes a laser diode serving as an emitter and a PIN diode providing optical to electronic signal conversion. These elements and the waveguide transducer comprise the sensing head. For applications involving insertion of the sensor head into harsh environments such as sediment layers, river beds and down well holes, protective packaging for the waveguide surface and the electronic components is required.

The current sensor package design occupies a total volume of 1 inch x 1 inch x 3 inches. The power source and signal processing electronics will be located remotely using two twisted wire pairs. The sensor head package will, however, house an optical source and detector as noted above and therefore must be sealed to prevent water and humidity penetration. In contrast, the waveguide surface must, however, be exposed to and simultaneously protected from physical damage by the sediment layers. To accomplish this, a separation membrane is supported between

two honeycomb mesh layers that provide mechanical support but simultaneously permits vapor transport. This structure has been shown to effectively protect the waveguide surface when exposed to harsh environments. In the mode of operation selected, the sensor functions by detecting BTEX vapors desorbed from the sediment or aqueous media. Direct detection of BTEX chemicals in aqueous media is difficult due to the low solubility of these species in water. As a result the organic species desorb into the chemical sensing layer but cannot be reabsorbed into the aqueous medium. Under these conditions the sensor response becomes basically irreversible.

In contrast, using vapor phase detection, the volume immediately adjacent to the sensing layer can be purged to ensure reversible operation.

Photomasks required for fabricating the two channel waveguide sensor have been received and actual waveguide fabrication has begun. Construction of the electronic housing package has also been initiated. Upon completion, the preliminary sensor package will be subjected to laboratory testing with sediment type materials. That testing is expected to be completed during next reporting period.

A-9416 # 7
E-20-X13

**DEVELOPMENT OF AN INTEGRATED-OPTIC INTERFEROMETER
FOR IN-SITU MONITORING OF VOLATILE HYDROCARBONS**

FINAL REPORT

Submitted to

U.S. Environmental Protection Agency
Region IV and VI
Hazardous Substances Research Center
Louisiana State University
Baton Rouge, Louisiana

Submitted by

James L. Walsh, Jr., GTRI/ESTL, Co-Project Director
Nile F. Hartman, GTRI/PSL Co-Project Director
Georgia Institute of Technology
Atlanta, Georgia 30332
404-894-8054 (for J. Walsh)

November 27, 1995

EXECUTIVE SUMMARY

This report summarizes the results of an investigation to develop and demonstrate a microsensor suitable for monitoring BETX chemicals. The underground storage tank (UST) provisions of the Resource Conservation and Recovery Act mandate that all USTs have leak detection by December 22, 1993. The problem of gasoline and other petroleum leaks from UST not only exist in the EPA Regions IV and VI states under the jurisdiction of the Hazardous Substances Research Center (HSRC), but are a national and international problem. Several of the methods acceptable to the U.S. Environmental Protection Agency (EPA) involve the use of sensors for detecting leaks in soil, sediment or water. One technique for accomplishing this detection measurement for gasoline storage tanks is to sense the presence of the BETX chemicals (benzene, ethyl benzene, toluene, and xylene). In addition, these four chemicals have been found at a large number of Superfund sites and are suspected to exist at even more. Although current laboratory instrumentation is satisfactory for chemical diagnostics, these instruments are of limited value for field monitoring applications due to size, cost and speed. Monitoring applications generally require real time, in-situ measurements using sensors that are 1) economically viable, 2) suitable for long term field operations, 3) easily maintained or repaired in the field and 4) require minimal fixed equipment for operation. Furthermore, new site investigations systems such as the cone penetrometer are being developed which could make use of microsensor technologies. This report summarizes the results of an investigation to develop and demonstrate a microsensor suitable for monitoring BETX chemicals.

The microsensor sensor technology is based on an integrated optic (IO), interferometric device capable of continuously measuring an individual chemical species in the ppmv or lower range. The sensor approach relies on the detection of very small refractive index changes in a thin film on the surface of an optical waveguide. Sensitivity to benzene, toluene and xylene have been demonstrated at concentrations in the low ppmv range. Further, the sensor technology has been shown to be capable of detecting the presence of gasoline in sedimentary soils. This technology offers the potential of monitoring several different chemical species on a single, multi-channel waveguide package only 1.5 inches in diameter and a few inches in length (including electronics). Moreover, techniques for negating many of the effects associated with a soil-water environment such as moisture changes, temperature variations, and chemical contamination have been developed and demonstrated. The sensor technology reported herein overcomes many of the disadvantages of existing techniques for measuring these substances including prohibitively high expense, excessively long measurement times, and inherently complex instrumentation that restricts field use.

The program was funded over a two year period at a total level of approximately \$148,000 plus approximately \$12,000 of cost sharing from GTRI. Concurrently, major funding from industry and other government agencies has been received to continue and expand the development of the sensor technology for soil and aqueous phase monitoring in environmental applications.

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1.0 INTRODUCTION

Key to environmental monitoring, restoration and remediation efforts is the development of suitable environmental diagnostic and monitoring capabilities. Government regulation formulated in the early 90's tend to reinforce the need for real time, in-situ sensors applicable to environmental monitoring. For example, the underground storage tank (UST) provisions of the Resource Conservation and Recovery Act mandated that all USTs have leak detection by December 22, 1993. Several of the methods acceptable to the U.S. Environmental Protection Agency (EPA) involve the use of sensors for detecting leaks in soil, sediment or water. One technique for accomplishing this detection measurement for gasoline storage tanks is to sense the presence of the BETX chemicals (benzene, ethyl benzene, toluene, and xylene). In addition, these four chemicals have been found at a large number of Superfund sites and are suspected to exist at even more. Although current laboratory instrumentation is satisfactory for chemical diagnostics, these instruments are of limited value for field monitoring applications as real time, in-situ measurements are required using sensors that are 1) economically viable, 2) suitable for long term field operations, 3) easily maintained or repaired in the field and 4) require minimal fixed equipment for operation. Furthermore, new site investigations systems such as the cone penetrometer are being developed which could make use of microsensor technology. This report summarizes the results of an investigation to develop and demonstrate a microsensor suitable for monitoring BETX chemicals.

1.1 Background

Subtitle I of the Resource Conservation and Recovery (RCRA) established the rules for the operation of underground storage tanks (USTs). These rules cover the registration, upgrading, monitoring, and other aspects of the operation of these systems. The requirements for release detection for all USTs are identified in Part 280.40 of Title 40 of the Code of Federal Regulations. Per these requirements, all USTs were to have release detection systems by December 22, 1993. These release detection systems were to have a probability of detection of 0.95.

The acceptable methods for leak detection are specified in Part 280.43. These methods include the following:

- Inventory control,
- Manual tank gauging,
- Tank tightness testing,
- Automatic tank gauging,
- Vapor monitoring,
- Groundwater monitoring,
- Interstitial monitoring, and
- Other methods.

The vapor monitoring, groundwater monitoring, and interstitial monitoring techniques all require the use of a sensing system. The current technologies used for these sensors include the following (API, 1989):

- Combustible indicators,
- Flame ionization detectors,
- Gamma radiation survey,
- Portable infrared spectrophotometer,
- Ultraviolet photoionization detector,
- Direct reading calorimetric indicating tube, and
- Oxygen meter.

Many of these current systems are expensive and the cost of using these systems for release monitoring would be prohibitive. The less costly systems such as the direct reading calorimetric indicating tube are not automatic and would present difficulties in actual operations. The need for automatic sensing systems is evident.

The problem of gasoline and other petroleum leaks from UST are not only a problem in the EPA Regions IV and VI states under the jurisdiction of the Hazardous Substances Research Center (HSRC), but are a national and international problem. In addition to detection of releases of gasoline from USTs, the IO sensor technologies could be used for detection of BETX chemicals from other waste sites and facilities. Zarrabi and Starks (1991) presented a survey of 546 sites on the superfund list indicating that benzene was found at 26% of the sites, ethylbenzene at 13%, toluene at 28%, and xylene at 13%. Therefore, an IO sensor developed for these four chemicals has application for other waste sites as well as release detection from USTs.

This report addresses the demonstration of a low cost, micro chemical sensor based on an integrated optic (IO), interferometric configuration (Hartman, 1990). The unique design of the IO interferometer eliminates or minimizes thermal and mechanical noise to provide a highly stable sensor platform for detecting very low concentration levels of contaminants in gaseous as well as aqueous environments. The sensor transduction relies on the detection of very small refractive index changes in a surface film. As in the bulk of the microsensors, specificity is achieved by using a thin surface film designed to be reactive or interactive with a selected chemical species or class or compounds. Relative to the fiber optic and surface acoustic wave techniques, the IO approach expands the list of potential surface film materials that can be used for detection of specific chemical species and, furthermore, offers improved detectability using those materials already developed for the fiber and acoustic techniques. While this technology offers all the benefits of the optical techniques, the IO optical circuit on a chip provides an expanded range of innovative sensor configurations for in-situ, real time chemical sensing applications. Specific advantages the IO sensor technology offers includes the following features:

- Active and passive sensing methods
- Very high detection sensitivities (ppbv to ppmv range)
- Fast response time (≤ 1 sec.)
- Small and compact sensor configurations
- Multiple channel/components sensing capabilities
- Nulling of interferant error signals.

In the following sections, the IO sensor technology is discussed and the laboratory results are presented.

2.0 TECHNICAL DISCUSSION

The integrated optic technology relies on planar waveguide structures rather than the more familiar cylindrical optical fiber waveguide configuration. A planar waveguide consists of a thin layer of slightly higher refractive index material deposited on the surface of a substrate of lower refractive index. Light coupled into this layer remains confined and will propagate through it. Direct access to the waveguide surface provides distinct advantages as thin film elements may be incorporated into or on to the waveguide surface to create two dimensional optical systems capable of performing all the functions of standard bulk optical systems. More importantly, access to the waveguide surface provides the basis for innovative sensor configurations relying on the interaction of a guided wave with a surrounding medium.

2.1. IO Waveguide Sensor

The chemical sensor configuration described herein relies on a planar optical waveguide structure operating in an interferometric mode. The integrated optic (IO) interferometer functions by sensing small refractive index changes resulting from the interaction of a species to be detected with a thin chemically selective film attached to the waveguide surface.

The interferometric configuration most applicable to commercial chemical sensing applications is a planar (non-channelized) version. Both single mode channel (Johnson, 1985) and planar multimode and single mode waveguide versions (Hartman, 1990) have been demonstrated. Only the planar version is well suited for real world applications due to the relative ease of coupling light into and out of the planar waveguide and fabrication advantages. An IO waveguide interferometer configured for chemical sensor operation is shown in Figure 1. In this configuration, the multimoded waveguide surface is covered with one or more thin strips of chemically selective agents designed to be interactive with the desired species to be detected. In operation, the evanescent field of a guided wave penetrates the waveguide/surface film interface, generating an exponentially decaying field in the surface film. As a result, refractive index variations within the surface film alters the phase of the guided beam through the evanescent interaction. The magnitude of the phase shift is easily determined by interfering the perturbed guided wave with an unperturbed guided reference wave and observing the fringe shift. In the multimoded waveguide version, the reference signal is provided by a low order guided optical mode while a higher order guided optical mode serves as the signal arm.

The evanescent field of a low order mode in a properly designed waveguide is tightly confined to the waveguide and so does not see changes in the cover film. In contrast, because the evanescent field associated with a higher order mode extends into the cover film, it is sensitive to index changes occurring therein.

The single mode version of an interferometric sensor operates on the same principles as the multimode but utilizes two guided beams spatially separated on the waveguide surface. In this instance, however, the waveguide is designed such that the evanescent field of both guided waves penetrates into the superstrate. One of guided beam path is covered with a chemically selective layer (signal beam) while the other is covered with an isolating layer (reference arm). Again, the interaction with the chemically selective film alters the phase of the guided beam under it and by interfering that guided wave with the reference beam, the chemically induced phase shifts are easily detected.

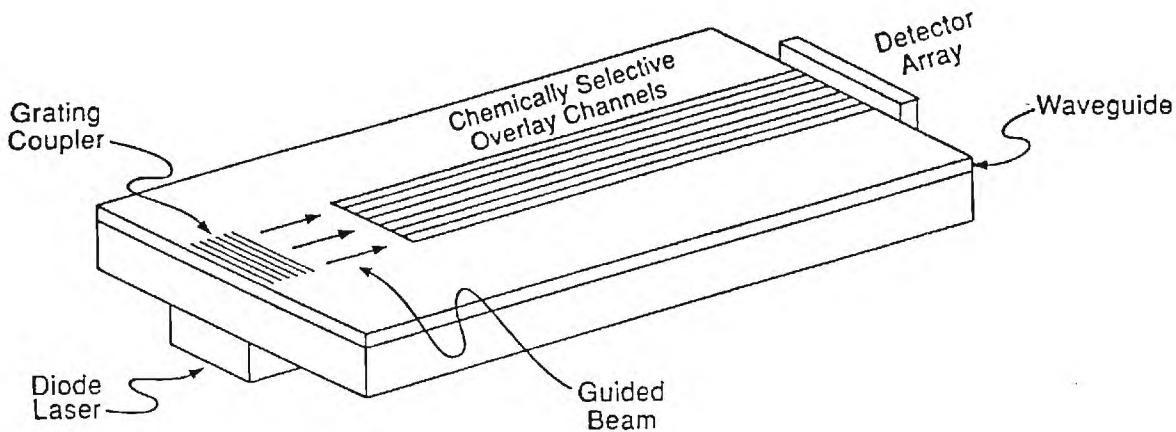


Figure 1. Multimoded waveguide interferometric sensor configuration.

2.1.1. Analysis and modeling

The interferometer operation may be described using a dispersion relationship relating step index waveguide parameters n_f (film index), n_c (cover film index), n_s (substrate index) and W (waveguide film thickness) (Tien, 1971). A convenient model for describing the interaction is based on the zig-zag ray model for the reflection of an optical ray between the two waveguide boundaries. The dispersion relationship can also be derived from an electromagnetic boundary value problem where a guided wave is confined by two dielectric boundaries. For ease of understanding and because both approaches yield the same result, only the ray model will be considered.

The dispersion relationship is defined by the "transverse resonance condition" which requires the sum of all phase shifts perpendicular to the direction of propagation in the waveguide to be a multiple of 2π ($2m\pi$ where $m = 0, 1, 2, \dots$) for one zig-zag period as shown in Figure 2. Thus the total phase shift associated with the transverse motion between the two boundaries must be an integer multiple of 2π for each full cycle. For one transverse passage through the waveguide, a phase shift of $kn_f W \cos \theta$ occurs.

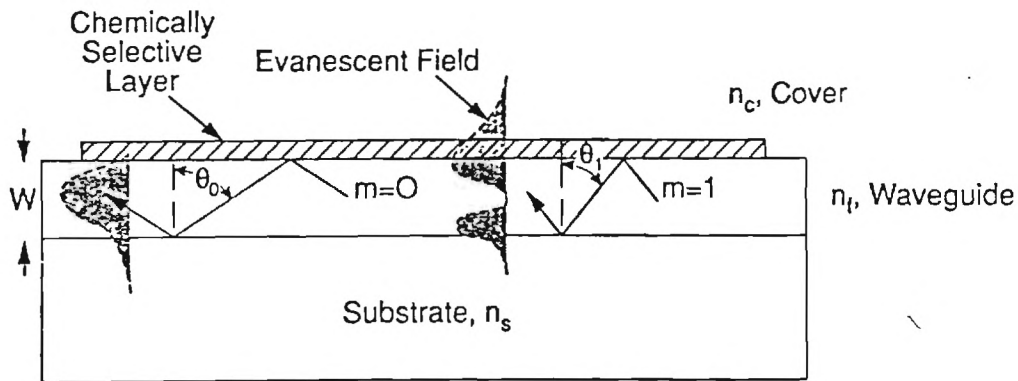


Figure 2. Ray model for waveguide analysis.

One full period however requires two transverse passages. Additionally, phase shifts of $-2\theta_c$ and $-2\theta_s$ occur due to total internal reflection at the surface and substrate boundaries of the waveguide. Thus the transverse resonance condition results in the following relationship for TE modes:

$$2kn_f W \cos \theta - 2\theta_c - 2\theta_s = m(2\pi) \quad (1)$$

$$\text{where} \quad \theta_c = \tan^{-1} \left[\frac{(n_f^2 \sin^2 \theta - n_c^2)^{1/2}}{n_f \cos \theta} \right] \quad (2)$$

$$\text{and} \quad \theta_c = \tan^{-1} \left[\frac{(n_f^2 \sin^2 \theta - n_s^2)^{1/2}}{n_f \cos \theta} \right] \quad (3)$$

Because the waveguide is thin and the index differences are small, waveguiding occurs only at discrete values of θ , with each angle corresponding to a propagating mode (m = mode number). The term $n_f \sin \theta$ in the previous equations is referred to as an "effective mode index" (N_{eff}), and represents an effective refractive index the waveguide material system exhibits for a propagating mode of a specific optical wavelength. Examining equations 1-3, if n_f , n_s and W are held constant while n_c is varied (i.e. a refractive index change in the cover medium due to a chemical interaction), then only θ may be varied to satisfy the equation. This change in the cover index manifest itself as a change in N_{eff} which is easily detected using interferometric techniques.

In practice, the minimal detectable change in N_{eff} is defined by the minimum phase shift detectable by the interferometer. The output of a waveguide interferometer operating at quadrature is described by the following equation;

$$I = \frac{I_o}{2} \left[1 + \cos \left[\frac{\pi}{2} + \frac{2\pi}{\lambda} L(\Delta N_{\text{eff}}) \right] \right] \quad (4)$$

where	I_o	=	peak intensity
	λ	=	free space wavelength of guided light,
	L	=	interferometer signal arm length,
	ΔN_{eff}	=	effective mode index change,
and	I	=	the output intensity of the interferometer.

With passive detection schemes, intensity changes of $\pm 0.1 I_o$ are easily detected at quadrature. This corresponds to a minimum detectable phase shift of 0.064π radians and a ΔN_{eff} of 10^{-6} . For a Si_3N_4 waveguide of 0.25 micrometer thickness and an optical pathlength of one centimeter on a fused silica substrate, this translates to a cover index change 2×10^{-6} . Sensitivities at this level are suitable for detection of organic species in the sub ppmv range.

3.0 EXPERIMENTAL RESULTS

3.1 COATING CHEMISTRY DEVELOPMENT

The chemical species selected from the BTEX group as target analytes include benzene, toluene, and xylene. Detection and monitoring capabilities depend on detection

sensitivity and specificity. The latter represents the most challenging problem because the organic species are small, simple molecules with similar chemical properties. The efforts in this program focused on realizing useful detection sensitivity levels and only demonstrating techniques for achieving class specificity.

Detection of the organic species of interest relies on absorption of target analytes into thin polymer coatings on the waveguide surface. The selected polymer coatings are designed to reversibly absorb the organic species to a greater or lesser extent, depending on the chemical nature of the polymer. The extent to which a particular organic species is absorbed by the coatings of each of the sensing channels, the magnitude of the polymer swelling, all in combination with the refractive indices of the analyte molecules and the polymers defines the magnitude of the index change resulting from the absorption process. In practice, the effective index change can increase or decrease, although, typically the effective index is observed to increase as polymer swelling tends to dominate (due to displacement of air with an index on $n = 1.00$ by a polymer with an index of ≥ 1.45). A number of polymeric materials were evaluated as candidate coatings. The screening process compared the relative response of specific polymer coatings and characterized the actual response (signal versus concentration in ppmv) for selected coatings. The screening process not only identified suitable coatings based on detection sensitivity but also provides the basis for selecting a combination of coatings (ie. sensing channels) to provide enhanced specificity.

Vapor phase measurements were utilized since this approach offers greatest flexibility where both sedimentary soils and aqueous phase environments will be encountered. In the case of sedimentary soils, the sensor can only detect the presence of trace vapors not bound to the soil molecules. In the case of aqueous environments, the relative solubility difference between water (very low) and the selective polymer layer (relatively high) limits the reversibility of the process. In practice, the dissolved organic species can come out of water and be absorbed by the selective polymer. The reversal process, however, is practically non existent at low concentrations. For measurements in the aqueous phase, a separation membrane, a hydrophobic filter, is required. The separation membrane also provides other advantages as it serves to protect the waveguide sensing surface from mechanical abrasion and contamination.

3.1.1 Waveguide Sensor/Coating Response

For the test measurements, air saturated with the organic species of interest was mixed with flowing nitrogen to dilute the flow impinging on the polymer coated waveguide surface. The phase change was then detected and the relative response determined based on the known vapor pressures for the organic species of interest. The waveguide element used for these experiments consisted of a fused silica (SiO_2) substrate overcoated with a 110 nanometer (nm) silicon nitride (Si_3N_4) waveguide film and a 40 nm fused silica film. The 40 nm fused silica layer only serves to provide different chemistries for attaching chemically active films to the waveguide surface.

The relative response of various polymer films to different organic species (in the vapor phase) is illustrated in Table I. The results are normalized to take into account the differing vapor pressures to permit a direct comparison of the relative sensitivities of the polymer films to a common species and the relative sensitivity to different species.

The larger numbers in Table I indicates higher sensitivity for the species tested. In particular Teflon AF (DuPont product and Trademark) exhibits good sensitivity to Toluene and Xylene. Conversely, poly(BIBMA) exhibits much better sensitivity to Xylene than to Toluene. Thus, while Teflon AF is an excellent candidate for sensitive detection of Toluene and Xylene, the addition of a second channel using poly(BIBMA) would provide a mechanism for discrimination between the two species.

TABLE I
RELATIVE SENSITIVITY OF POLYMER FILMS

^a <u>Polymer Film</u> <u>Vapor Phase Species</u>	Phase Shift (π radians) ^d			
	<u>Poly(vinyl acetate)</u>	<u>Poly(BIBMA)^b</u>	<u>Poly(SBMA)^c</u>	<u>Teflon AF</u>
Toluene	2.0	2.5	1.0	6.0
Xylenes	4.5	6.1	1.25	6.25
Acetone	1.0	0.25	0.1	3.0
Methanol	3.0	0.3	<0.1	1.5
Water/Air	1.25	1.0	<0.5	<0.5
Methylene Chloride	3.5	0.25	0.2	1.25
Chloroform	2.5	0.5	0.7	7.5
Carbon Tetrachloride	2.0	0.5	0.35	2.0

a. Saturated vapor diluted into steam of nitrogen

b. poly(butyl-isobutyl methacrylate)

c. poly(styrene)-poly(butyl methacrylate) copolymer ([thick film])

d. normalized to 100 mm Hg vapor pressure of injected vapor

The response of a coated waveguide to toluene and benzene is presented in Figure 3. The selective polymer was a 100 nm thick poly(isodecyl)methacrylate film and the waveguide was a 110 nm thick Si_3N_4 film on a fused silica substrate. The overall sensitivity is dependent on several factors including;

- waveguide design and parameters
- polymeric coating
- polymer thickness
- sensing channel length.

The results presented in Figure 3 do not represent the optimum performance for this combination. In particular, the sensing polymer film thickness was very thin, approximately 100 nm, and the total sensing pathlength was only 1.8 cm. With increasing pathlength, the sensitivity would increase linearly. Increasing the polymer film thickness offers the potential for significant increase in sensitivity.

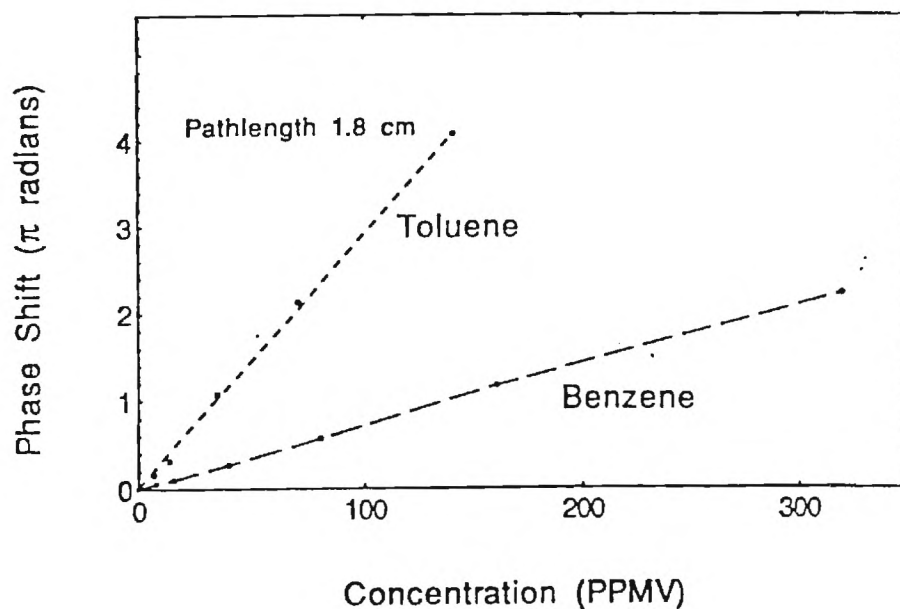


Figure 3. Sensor response to toluene and benzene.

Although increasing the thickness of the chemically selective polymer film thickness can increase detection sensitivity, the time dependent response will be slowed since the process is controlled by diffusion of the vapors into the film. The time dependent response of the 100 nm thick film is quite fast as Figure 4 illustrates. The result shown in Figure 4 was

generated by introducing a "puff" of air saturated with the vapor. In practice, the time dependent response of the sensor is much faster than the dynamics of the gas flow. Thus the actual response being measured is the gas flow dynamics of the delivery system.

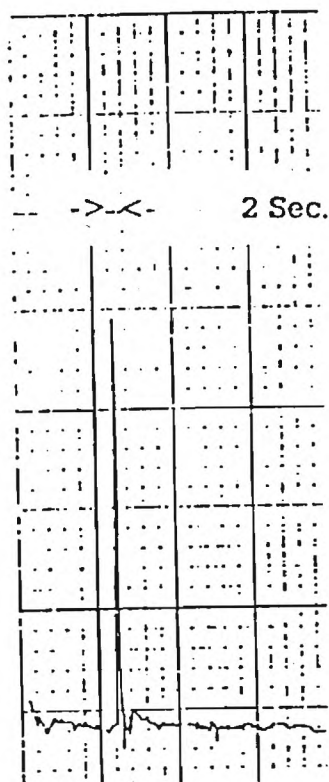


Figure 4. Sensor Time Dependent Response.

3.1.2 Sensor Response for Contaminated Sedimentary Soil Samples

To test the sensor response using contaminated sedimentary soils, the configuration illustrated in Figure 5 was used. The waveguide was identical to that described previously while the polymer film used was poly(SBMA) described in Table I. For test purposes, the soil sample was contaminated with small sample volumes of gasoline and toluene. The response of the sensor was recorded as function of time. The time dependent response is strictly defined by the diffusion of the specimen through the thickness of the sediment layer which was 1 cm. The specimen, having a volume of approximately 1 microliter, was placed directly on the top surface of the sediment for these test. A response typical of that presented in Figure 6 was observed indicating the detected presence of the contaminant for both gasoline and toluene. Note the detected signal is extremely large in comparison with the minimum detectable signal of 0.01π radians. The slow recovery time (full recovery required 30 minutes) occurs because the test species as released from the selective polymer film was entrapped.

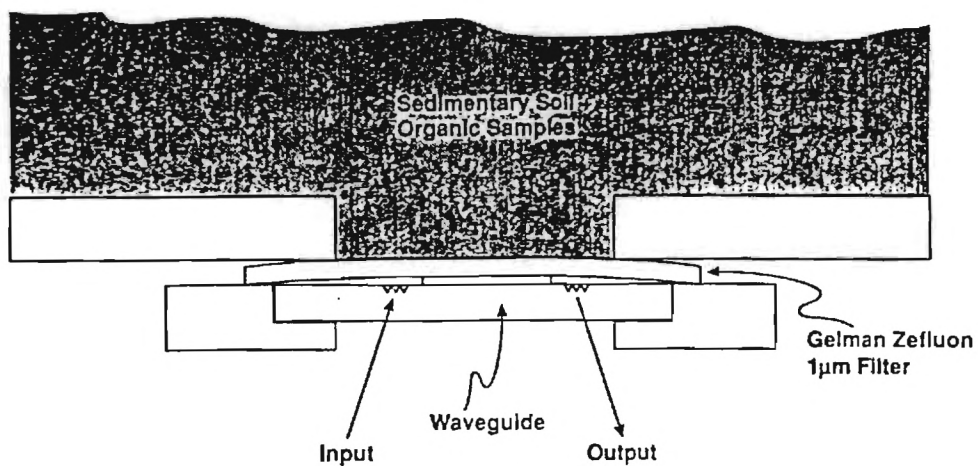


Figure 5. Laboratory test bed for sedimentary soil testing.

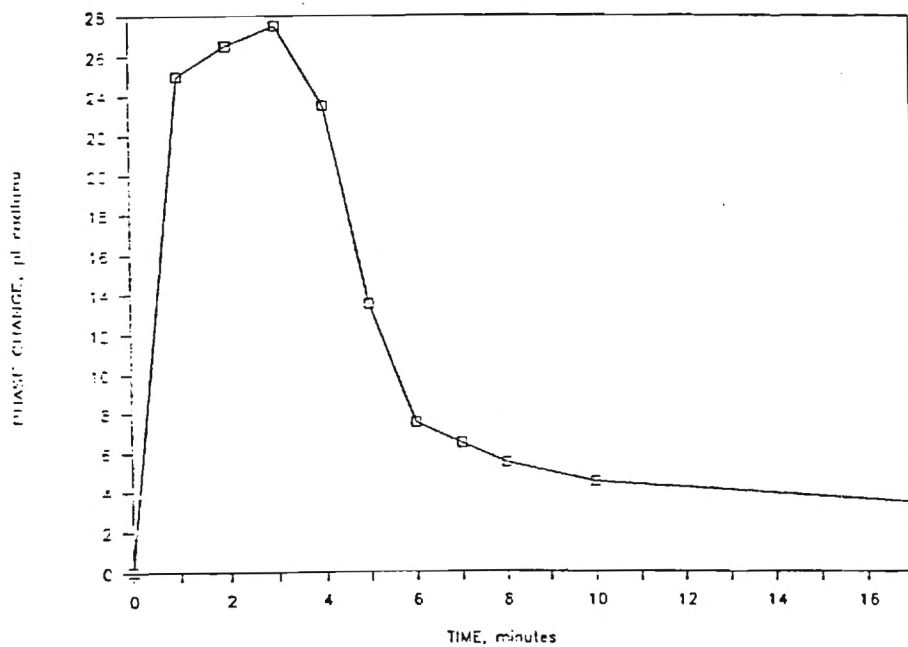


Figure 6. Sensor response to the introduction of toluene into sediment sample.

3.1.3 Waveguide Surface Protection.

Because the waveguide surface is sensitive to mechanical abrasion and its throughput can be attenuated by opaque residue deposited directly on the waveguide surface, the sensing surface must be protected. As noted previously, a separation membrane was used as a means of overcoming the lack of reversible absorption observed in an aqueous media. The membrane offers further advantage in that it aids in the protection of the surface. To further enhance protection, the entire waveguide surface was fluorinated. The latter tends to reduce binding of residue to the waveguide surface.

The waveguides were tested in terms of survivability in a variety of aqueous environments. In particular, the most harsh condition included a flowing stream at a temperature of approximately 60 °C and a pH of 10.6. Under these conditions, damage to the waveguide was observed when the waveguide surface was exposed directly to the hot, caustic media. The damage was included actual etching and destruction of surface films. In the case of dry soil samples, the hydrophobic filter provided adequate protection against dust contamination.

3.2 SENSOR PROBE DESIGN AND CONFIGURATION

Although a complete prototype sensor system suitable for field testing was not part of the two year effort, through synergism with other projects a prototype system has been developed. The probe configuration is compatible with the design requirements for the cone penetrometer. Although specific details of the probe design are proprietary, the overall configuration and package is illustrated in Figure 7. The basic waveguide configuration is illustrated in Figure 8. The optical source is a diode laser. Grating couplers are utilized to couple light into and out of the waveguide. PIN diodes are utilized for light detection. The sensor shown in Figure 7 includes four sensing channels.

4.0 FUTURE DEVELOPMENT PLANS

A significant funding base has been secured to ensure the development of the sensor system for environmental applications. The funding base includes heavy participation by industrial firms, enhancing the probability of commercialization. Specific programs include the following activities:

"An Integrated Optical Chemical Sensor for Cone Penetrometers"

Funding Agencies: Army Research Office and industry

"E-Smart System for Environmental Monitoring"

Funding Agencies: ARPA and industry

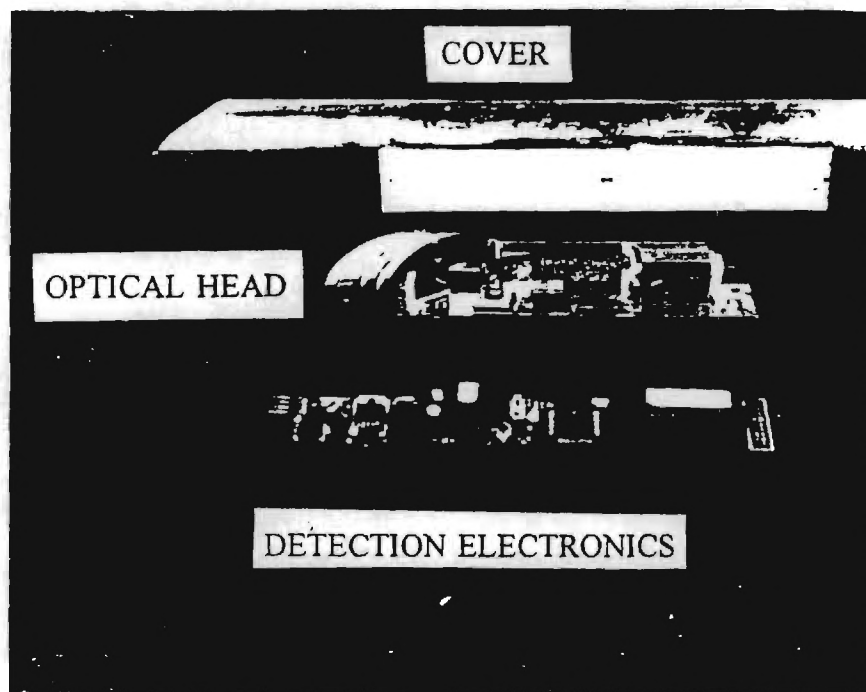


Figure 7. Prototype sensor package including optics, detection electronics and housing.

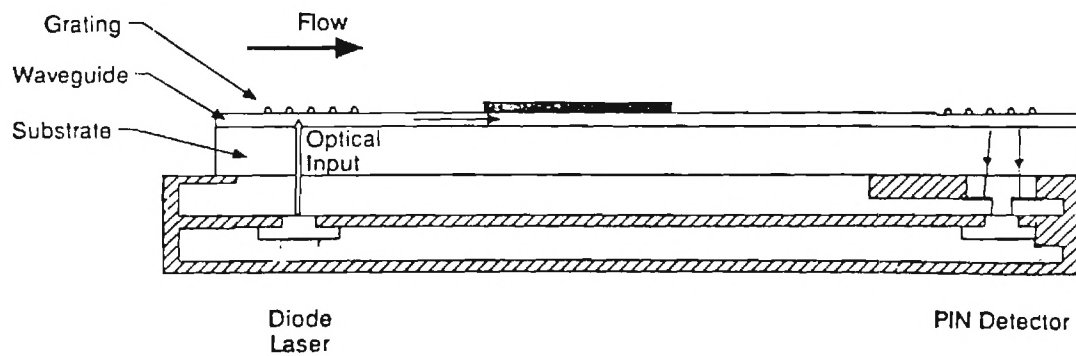


Figure 8. Crosssection of sensor head configuration.

5. SUMMARY

A microsensor sensor technology based on an integrated optic (IO), interferometric device capable of continuously measuring an individual chemical species in the ppmv or lower range has been demonstrated. The sensor approach relies on the detection of very small refractive index changes in a thin film on the surface of an optical waveguide. Sensitivity to benzene, toluene and xylene have been demonstrated at concentrations in the low ppmv range. Further, the sensor technology has been shown to be capable of detecting the presence of gasoline in sedimentary soils. This technology offers the potential of monitoring several different chemical species on a single, multi-channel waveguide package only 1.5 inches in diameter and a few inches in length (including electronics). The sensor configuration evolving from this program is ideally suited for cone penetrometer use. Moreover, techniques for negating many of the effects associated with a soil-water environment such as moisture changes, temperature variations, and chemical contamination have been developed and demonstrated. The sensor technology reported herein overcomes many of the disadvantages of existing techniques for measuring these substances including prohibitively high expense, excessively long measurement times, and inherently complex instrumentation that restricts field use.

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