

## USE OF A REAL-TIME SENSOR SYSTEM TO REDUCE THE COSTS OF ENVIRONMENTAL RESTORATION

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### ABSTRACT

The Department of Energy's costs for environmental monitoring, restoration, and associated liabilities can be dramatically reduced through technologies that provide real-time, autonomous and affordable field data that are vital for environmental restoration efforts. The Georgia Tech Research Institute (GTRI) has pioneered applications of sensor technology through the research and development of a cost-effective environmental sensor system for the field detection and measurement of chlorinated and aromatic compounds and other aqueous chemical and biological monitoring data. The sensor, an integrated optic planar waveguide interferometer is designed to collect real-time, chemical-specific data from gases and liquids. Judicious choice of polymer films allows for the detection of virtually any environmental contaminant. Field tests have detected low part per million levels of trichloroethylene (TCE) from groundwater samples within minutes of sample collection. The data correlates well with laboratory results obtained from gas chromatography/mass spectrometer methods. In lab calibration measurements of the sensor, projected detection limits for the sensor are in the low part per billion levels.

Some of the advantages of this sensor system for environmental applications are its low initial and per-sample cost, the ability to detect multiple analytes simultaneously, and the speed and sensitivity of detection. Systems can be designed for mobile, on-site field analysis with instant results or in-situ monitoring with automatic data logging and communication to a base site.

### INTRODUCTION

The Department of Energy will spend billions of dollars during the next decade for environmental monitoring and restoration programs in the United States. These programs are typically driven by cleanup standards for relatively few compounds, such as trichloroethylene (TCE). Sample collection and laboratory analyses for cleanup compounds alone result in annual DOE expenditures of hundreds of millions of dollars. This paper describes the use and applications of a real-time sensor system to reduce DOE's environmental restoration costs. GTRI has developed an optical sensor capable of detecting a wide variety of chemical and biological species. GTRI's sensor system has been field tested. The sensor is fast, highly sensitive and provides a direct measurement with no additional steps or consumable reagents. Many of the sensor's components are inexpensive and off-the-shelf including a laser diode light source and CCD detector. Costs for the sensor are in the sub \$500 range. In addition to reducing costs, the sensor provides opportunities for advancing research for monitored natural attenuation/enhanced passive remediation (MNA/EPR) scenarios by allowing the real-time measurement of microbial and chemical processes in the natural sub-surface environment.

### THE OPTICAL SENSOR

At the heart of the optical sensor is a planar optical waveguide. Planar waveguides are related to fiber optic waveguides in that a high refractive index material is used to guide the light within its confines through total internal reflection. Whereas a fiber optic's high refractive index core is surrounded by a lower refractive index cladding, the planar waveguide has the high refractive index waveguiding layer deposited on top of a lower refractive index planar substrate, such as a piece of glass with the top side of the waveguide exposed. Planar waveguides have evanescent fields, the tail of the electromagnetic field associated with the propagation of light, sensitive to index of refraction changes in the volume immediately above the waveguide surface. These fields extend up to 500 nanometers (nm) above the surface. Placing a chemically sensitive film within this region provides the basis for the chemical sensor (Fig. 1).

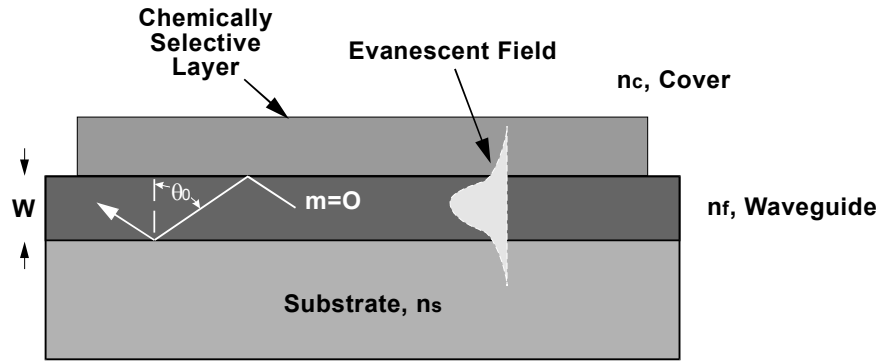


Fig. 1 Diagram for single mode waveguide with buried evanescent field

Sensing chemistries can be tailored to respond to an endless variety of chemical agents, toxic industrial chemicals, and biological materials. When chemical or physical changes occur in the sensing arm, the velocity of the propagating light beam will change. To measure this change, a reference beam, propagating adjacent to the sensing beam, is optically combined with the sensing beam creating an interference pattern of alternating dark and light fringes. A change in the interference pattern is measured using a Fourier transform algorithm. With detection sensitivities on the order of 0.05 radians, index changes of less than  $10^{-6}$  can be measured [1-3]. The sensing mechanism can be passive (a physical change) or active (chemically reactive sites in the film) depending on the target analyte. Chemical sensing films typically consist of polymer films, which are thick enough, 500 nm, to bury the evanescent field and thereby shield the sensor from unwanted environmental effects such as dirt and bubbles.

The optical waveguide sensor chip consists of a 160 nm layer of silicon nitride ( $\text{Si}_3\text{N}_4$ ) deposited on a piece of BK-7 glass. Grating couplers for coupling the light into and out of the waveguide are fabricated into the underlying substrate before the waveguiding layer is added. A thick, 500 nm, layer of silicon dioxide ( $\text{SiO}_2$ ) is deposited over the entire waveguide except in the channels where the sensing polymer will be deposited. The  $\text{SiO}_2$  layer shields the guided beam from any undesirable environmental effects allowing only the response from the sensing polymer to be of consequence. The current chips are approximately 1 x 2 cm in size and 1 mm thick. With interferometers being only a fraction of a millimeter in width, several interferometers (sensors) can be placed on a single chip. A diode laser illuminates all channels across the width of the input grating. Channel lengths are defined by patterned thick  $\text{SiO}_2$  and are typically 1.5 cm. Multiple polymers employing various sensing mechanisms can be deposited on the different interferometers and used to provide a patterned output for analyte identification and concentration determination. Field testable sensor units have been assembled (Fig. 2), and electronics and software have been developed to convert interferometric signals into total phase shift and concentration.

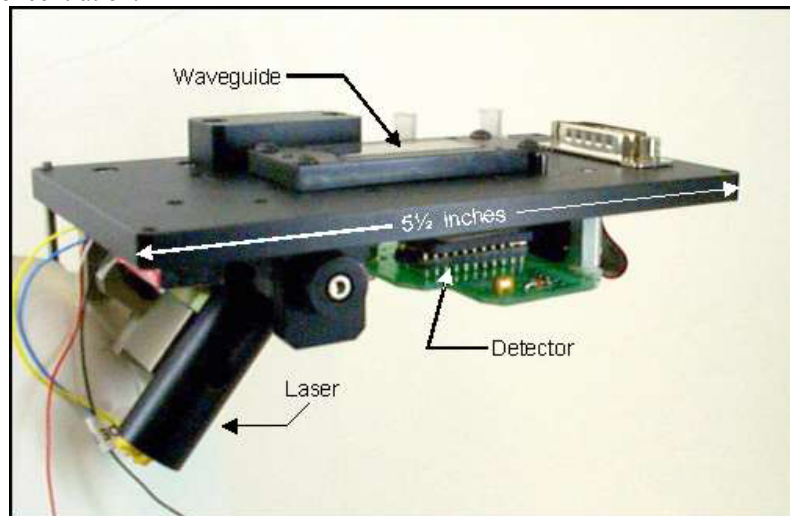


Fig. 2 Current sensor prototype

## SENSING CHEMISTRY

Owing to the low reactivity of TCE, perchloroethylene (PCE) and the natural degradation products of these two solvents, *cis*- and *trans*-dichloroethylene (DCE) and vinyl chloride, the sensing mechanisms employed for their detection are passive in nature. Typically, these sensing films consist of one or more polymer or sol-gel layers. Passive chemistries rely upon the sensing layer absorbing the analyte and physically changing (swelling, filling of void volume or dissolution)[4]. Swelling dominates the response when the polymer film is thinner than the evanescent field. Analyte absorption swells the polymer film vertically further into the evanescent field, which always appears as a positive change in index (a negative change in phase). This mechanism is undesirable because the exposed evanescent field is also sensitive to environmental background (e.g. bulk index changes, scattering and adsorption of particulate or colored matter.) The alternative mechanisms, void volume filling and dissolution, allow one to shield the evanescent field from such effects using films thicker than the evanescent field.

Filling of void volume occurs with polymers having glass transition temperatures ( $T_g$ ) above the operating temperature. The analyte penetrates interstitial volume between rigid polymer chains. As long as the polymer is insoluble in the analyte, only this mechanism will be observed with high  $T_g$  polymers, such as Teflon AF<sup>®</sup> (TAF). The index change for the film and analyte is again a positive index change, producing a negative phase change.

The third possible mechanism is dissolution occurs when the polymer has a  $T_g$  lower than the operating temperature. As a low  $T_g$  polymer contains no void volume for the analyte to fill, the analyte must dissolve into the polymer. Depending on the index of refraction of the analyte and polymer, the composition index can be negative, positive, or zero (if the polymer is index matched to the analyte), this provides for discrimination of analytes. Two separate interferometers with polymers with different refractive indexes are needed to distinguish the difference between a small amount of an analyte with a large polymer/analyte index difference and a large amount of analyte with a small polymer/analyte index difference. Figure 3 shows the dissolution responses of a series of methacrylate/acrylate polymers (with refractive indices of 1.41, 1.48 and 1.52) to benzene, toluene, and chlorinated solvents in aqueous solution. For the low index polymer, all analytes increase the overall index, while the opposite is seen in the high index polymer. In the middle index polymer the response of the chlorinated solvents are opposite that of the aromatic analytes. By grouping several different polymers on a series of interferometers, a patterned response is obtained which will allow chemometric analysis of the data to identify and quantify the analytes present.

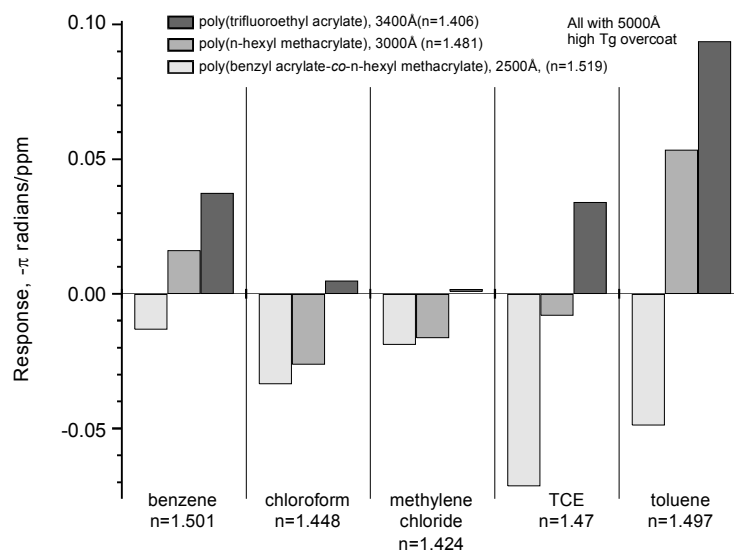


Fig. 3 Effect of polymer refractive index on response to aqueous analytes

In aqueous solution the magnitude of steady-state response for a given analyte is a function of the analyte's concentration, its partition coefficient and the index of refraction difference between the analyte and the polymer. However, the time required to reach steady-state is driven primarily by the partition coefficient. When the partition coefficient is large, more extractions of the solution containing analyte by the polymer are needed to reach equilibrium. For the reverse process, the extraction out of the polymer by a solution containing little or no analyte will take longer for high partition coefficient analytes. Because these films are always very thin (< 1 micron), the volume of polymer is very small compared with the solution above it. Since the number of extractions per unit time is large, equilibrium is reached in a reasonably short time. Sensitivities are in the <100 part per billion (ppb) range for the aromatic and chlorinated hydrocarbons tested.

## FIELD DEMONSTRATION RESULTS

For screening and calibration of candidate sensing polymers and initial field tests, a single interferometer sensor chip was used. The polymer was applied by dip coating the chip into a solution of the polymer and slowly withdrawing. Thicknesses of the polymers were measured by profilometry and typically were in the 500-700 nm range. After mounting the chip on the sensor platform and attaching a flow cell, a flow of deionized water was started. After achieving a stable baseline, the chlorinated analyte was injected into the stream at a known rate to yield the concentration desired. An in-line UV spectrometer provided verification of the concentration by measurement of TCE absorption at 200 nm. Figure 4 shows the response of the sensor to various concentrations of TCE using TAF as the sensing film. From this data a calibration curve is obtained, which for TAF was linear with concentration (not shown).

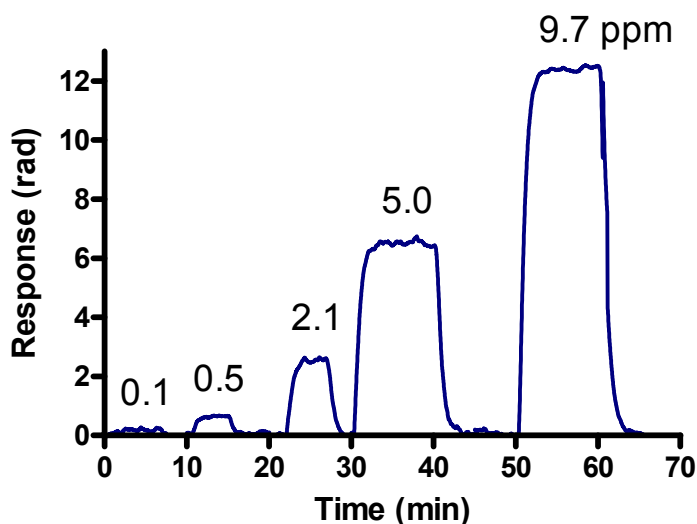


Fig. 4 Response of Teflon AF film to aqueous TCE

Another polymer, poly(2,6-dimethyl-1,4-phenylene oxide (PDPO), showed even greater sensitivity to TCE and PCE with the response being nonlinear; lower concentrations gave greater relative responses. The results from PDPO for various analytes at 1 ppm concentrations are presented in Table I. The response of PDPO is much greater for TCE and PCE compared to TAF and projects a limit of detection for these analytes in the low ppb to high part per trillion (ppt) range.

Table I Response to PDPO sensing film at 1 ppm concentration of various organic analytes

Analyte	Response in radians
TCE	257
PCE	240
Methylene Chloride	2.4
Chloroform	1
Toluene	153
Benzene	59

Recently, the sensor was field tested at a major industrial site with significant contamination of groundwater by TCE. Sensor tests were performed in parallel with conventional sampling and analysis. Repeated injections of groundwater from several monitor wells were conducted. The sensor responses were converted to TCE concentration, based on laboratory calibration data, and averaged over multiple injections for each well. The average concentrations, as well as data obtained from standard analytical techniques for TCE, EPA Method 8260, are shown in Table II. Table II also shows the change recorded at the four different wells over a two-month time interval. In all cases, the concentration measured using the sensor follows the trend of the analytical results but was consistently higher. We believe that this is due to the unavoidable loss of TCE during standard groundwater well sampling techniques and the necessary transfers and sample manipulations involved in laboratory analysis.

Table II TCE Concentrations in ppm Measured with the Sensor and by Analytical Method (EPA 8260) from Different Wells in March and May of 2003

Well	March-03		May-03	
	Sensor	Analytical	Sensor	Analytical
1	4.3	2.6	2.3	2.3
2	3.0	1.0	2.5	0.94
3	3.0	1.4	2.3	1.0
4	6.1	3.2	5.4	2.0

## CONCLUSIONS

Optical sensor systems for groundwater and surface water monitoring have been successfully tested. Detection of sub-ppm concentrations of organic constituents in real-time and reversibly has been demonstrated. By tailoring the chemically sensitive layer, the sensors can be adapted to virtually any chemical or biological analyte. Detection limits in the low part per billion range are possible for select compounds.

The integrated optic interferometric sensor fits the need for real-time, in-situ groundwater and surface water monitoring of TCE and should be applicable to other organic contaminants. Deployment of real-time sensor systems could significantly reduce the characterization and long-term monitoring costs associated with environmental restoration programs. Continuous real-time water quality data not previously available to environmental managers and researchers allows for the collection of virtually thousands of data points per year, compared to the annual four data points derived from typical quarterly sampling programs. In-situ sensors also may serve as "sentinel" monitoring points at or near the fringes of a contaminant plume, thereby providing a strategic tool for plume containment and environmental protection. Future work is directed toward continued polymer testing, software development for species identification and quantification, and a remote data transmission and communication interface.

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