EPA Grant Number: R819165-01-0

Title: Development of an Integrated Optic Interferometer for In_Situ Monitoring of Volatile Hydrocarbons

Investigator(s): J. Walsh [1], N. Hartmann [1]
Institution(s): HSRC/S&SW, [1] Georgia Institute of Technology
Center Director: L. J. Thibodeaux
EPA Project Officer: Dale Manty
Project Period: 1992-1994
Project Amount: $172,100

Objectives/Hypothesis

In this project a microsensor was developed and demonstrated which was suitable for monitoring BETX (benzene, ethylbenzene, toluene and xylene) chemicals. 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 pplications 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.

Approach

The microsensor 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.

Results

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.

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. 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.

Waveguide Sensor/Coating Response

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.

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 overall sensitivity is dependent on several factors including; 1) waveguide design and parameters, 2) polymeric coating, 3) polymer thickness, and 4) sensing channel length.

Sensor Response for Contaminated Sedimentary Samples

To test the sensor response using contaminated soils a soil sample was contaminated with small sample volumes of gasoline and toluene. The response of the sensor was recorded as a 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. The typical response was a high detected phase change signal between the first and fourth minute of the test for both gasoline and toluene. The slow recovery time (full recovery required 30 minutes) occurs because the test species as release from the selective polymer film was entrapped.

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 previously noted, a separation membrane was used as a means of overcoming the lack of reversible absorption observed in an aqueous media. The waveguides were tested 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 included actual etching and destruction of surface films. In the case of dry soil samples, the hydrophobic filter provided adequate protection against dust contamination.

Sensor Probe Design and Configuration

Although a complete prototype sensor system suitable for field testing was not a part of the HSRC funding effort, through synergism with other projects a prototype system was developed. The probe configuration is compatible with the design requirements for the cone penetrometer.

Summary of Results

- Developed and demonstrated device for detecting BTEX
- Instrumented device in cone penetrometer application
-

Supplemental Keywords

BTEX, microsensor, and detection

Students Supported

A. Umesh (PhD)

Publications and Presentations

Hartman, N.F., "Dual Use Roles for Optoelectronic Technologies in Military and Industrial Applications", Dual Use TECHNOLOGIES and APPLICATION Conference, SUNY Institute of Technology, Utica, New York, May 23_26, 1994.

Research Brief #4: Developing a Sensor to Find and Monitor Contaminants In Situ (1994)

Walsh, J. and N. Hartman, "Development of an Integrated-Optic Interferometer for In Situ Monitoring of Volatile Hydrocarbons", Final Project Report submitted to the South and Southwest Hazardous Substance Research Center, November 1995.

Walsh, J. L., C. C. Ross, N. F. Hartman, “Sensors can find and monitor contaminants”, *Centerpoint,* Vol. 1, No. 1, 1993, p. 10.

For Further Information

Dr. Danny Reible
E-mail: reible@lsu.edu