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A FIBER-OPTIC SENSOR SYSTEM FOR MONITORING CHLORINATED HYDROCARBON POLLUTANTS

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Summary—We have developed and field-tested a fiber-optic chemical sensor system for use in environmental monitoring and remediation. The system detects chlorinated hydrocarbon pollutants with colorimetry, and is based on an irreversible chemical reaction between the target compound and a specific reagent. The reaction products are detected by their absorption at 560 nm and can be monitored remotely with optical fibers. Continuous measurements are made possible by renewing the reagent from a reservoir with a miniature pumping system. The sensor has been evaluated against gas chromatography standards and has demonstrated accuracy and sensitivity (5 ppbw) sufficient for the environmental monitoring of trichloroethylene and chloroform. Successful preliminary field tests have been conducted in a variety of contamination monitoring scenarios.

Because of increased governmental and public concern over the extent of subsurface contamination, considerable effort has been recently directed towards developing enhanced monitoring capabilities for compounds of toxicological interest. Our work at Lawrence Livermore National Laboratory (LLNL) has focused primarily on two of the more important chlorinated hydrocarbon pollutants: chloroform and trichloroethylene (TCE).[1] We have developed a fiber-optic-based sensor technology to measure these compounds both quantitatively and remotely. Optical fibers are used to detect formation of colored products in specific transparent reagents upon exposure to target compounds. The chemical reagent used is an outgrowth of the work of Fujiwara, who first demonstrated that basic pyridine, when exposed to certain chlorinated compounds, develops an intense red color.[2] This red color is due to formation of highly conjugated molecules that exhibit strong absorption in the blue-green region of the spectrum (Fig. 1). By monitoring the rate of color formation in a specially designed sensor, we are able to detect and quantify certain chlorinated hydrocarbons at very low concentrations.

EXPERIMENTAL

Fiber-optic sensor system

Basic components of the fiber-optic sensor system include a reagent delivery assembly consisting of supply and waste reservoirs and a pumping and metering capability, the sensor, an electro-optic readout consisting of a silicon photodiode (Hamamatsu S-1133-14) detector and either an incandescent lamp and band-pass filters or a 555-nm LED, and a computer for control and data reduction (Fig. 2).

The sensor was comprised of two optical fibers, two capillary tubes for reagent transfer, and semipermeable membrane tubing (Fig. 3). The input fiber was 400 μm ϕ glass on glass Mitsubishi ST-400-E-SY or 400 μm ϕ glass on glass 3M-FG 400 LAT. The output fiber was 200 μ ϕ glass on glass Mitsubishi ST 200D SY. An optical fiber and reagent tube were sealed in each of two stainless-steel tubes. These tubes were then slip fitted to semipermeable membrane tubing, which was subsequently held in place by heat-shrink tubing. The resulting assemblies were made parallel and housed, along with the thermistor, in a larger stainless-steel tube, giving the sensor its loop configuration. Light emitted from the delivery fiber was collected by the return fiber only by scattering inside the body of the white porous membrane tubing. Approximately 0.001% of the incident light was collected with an unexposed, reagent-filled membrane. When the porous tube was exposed to target vapors, the organohalide compounds diffused readily through the membrane and formed a colored product on the inside walls of the tubing. This color significantly

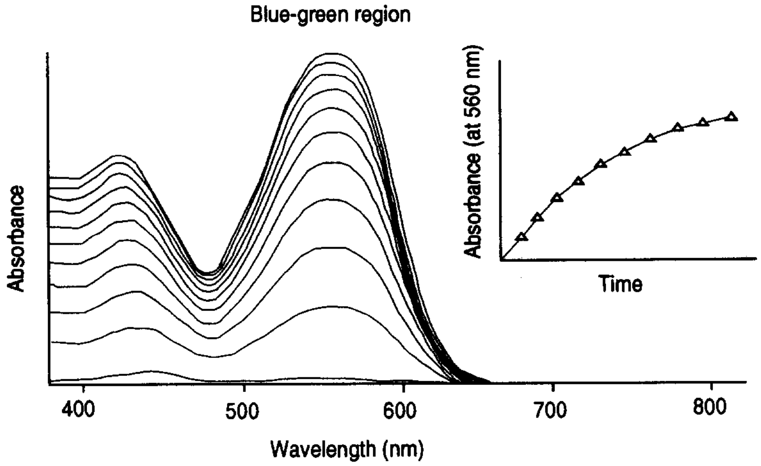


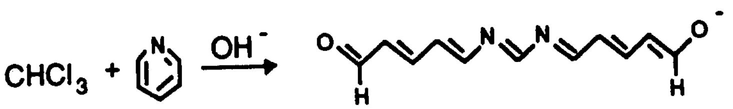
Fig. 1. The visible-light absorbance spectrum of the Fujiwara reaction of pyridine with certain chlorinated compounds shows strong absorption in the blue–green region. Measurement is based upon monitoring the absorbance increase with time at 560 nm of a sequestered reagent exposed to hydrocarbon vapor.

reduced the transmission of visible light through the sensor and thus provided for the sensitive measure of the target compound.

Chemical reagents

Basic pyridine, when exposed to certain chlorinated compounds, develops an intense red color due to the formation of highly conjugated product molecules. This reaction, first identified by Fujiwara, has long been the basis for the detection of organochlorides by colorimetric techniques.[2]

Although the mechanism for the color forming reaction has not been rigorously proven, the overall reaction sequence that leads to the colored products has its foundation in the chemistry of N-alkylated pyridines. For each step in the reaction, there can generally be found analogous documented reactions of alkylated pyridines exhibiting similar reactivity and yielding products of corresponding structure.[3] The development of selective indicator reagents for specific chlorinated compounds was centered on the reactivity of the volatile analytes. The



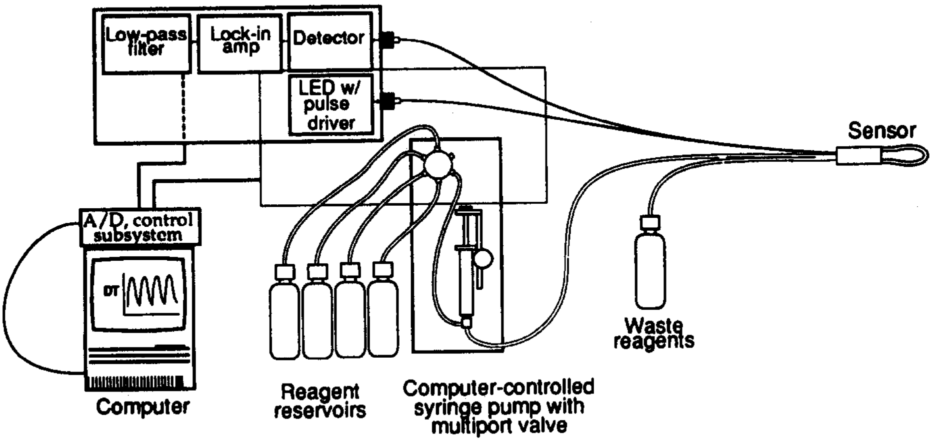


Fig. 2. A bench-top version of the fiber-optic sensor system with an electro-optic readout consisting of either an incandescent lamp and band-pass filters or a 555-nm LED.

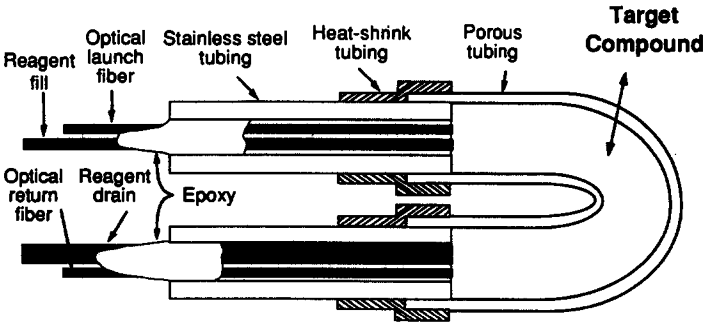


Fig. 3. The colored product of reagent and target compound is shown as shading on the inside walls of the porous tubing of the loop sensor.

reaction of chloroform and trichloroethylene in the presence of strong base leads to formation of reactive intermediates that are the agents most likely responsible for the initial N-alkylation of pyridine. Chloroform reacts with base to form dichlorocarbene (:CCl_2) and TCE undergoes 1,2-dehydrochlorination to give dichloroacetylene ($Cl—C{\equiv}C—Cl$). Both these intermediates are extremely reactive toward nucleophiles such as pyridine.

Based on the varying reactivity of the organohalide analytes, we designed reagents that provide some degree of selectivity to, and sufficient sensitivity for, TCE and chloroform. For TCE, the optimum reagent was 99% pyridine (by volume) and 1% tetrabutyl ammonium hydroxide (TBAH) (40% aqueous solution by weight). For chloroform the optimum reagent was 87.5% pyridine and 12.5% TBAH.

Reagent delivery

Because the chemical reaction is irreversible, repeat measurements require flushing the sensor membrane tube and delivering fresh reagent. Following the work of Berman *et al.*,[4] we developed several novel ways to provide fresh reagent to the sensor. Our most versatile delivery system used an encoded DC motor and gear head that were put in line with a drive screw and two identical, gas-tight 5-ml syringes (Fig. 4). One syringe served as the reagent reservoir and the other as the collector for spent-reagent. The motor turned the drive screw, which moved an actuator nut along its length. The actuator was fixed to the syringe plungers, which were juxtaposed, thereby dispensing one syringe while simultaneously retracting the other. In a closed loop with a sensor, this system can deliver fresh reagent on demand without any net increase in pressure within the sensor body. Its high aspect-ratio structure also permitted us to enclose it in a variety of ground-penetrating devices such as a penetrometer cone (1.25-in. i.d.) or monitoring well packing assemblies and, therefore, gain easy access to the subsurface or groundwater.

Calibration

To calibrate, we placed the sensor in the headspace of a gas-tight sampling vessel (typically a 250-ml Pyrex jar with a custom valve fitting) that contained a solution of the target molecule at a known concentration. The solution was stirred for several minutes to ensure equilibrium between the headspace and aqueous phases. Six measurements, 2.5 min in duration, were then taken for each concentration.

A slope was calculated for each measurement using a uniformly selected linear interval on the positive slope of each absorbance curve t_1–t_2 (Fig. 5). The average of six slope values taken at each concentration was then plotted against its input concentration (w/v as calculated from

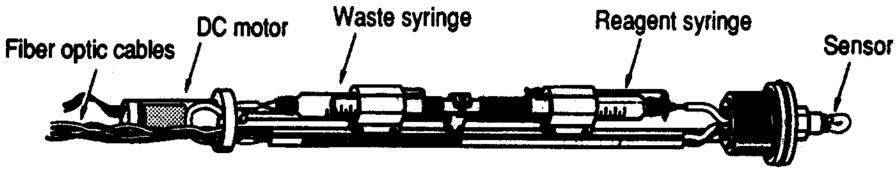


Fig. 4. The high-aspect ratio reagent delivery system provides fresh reagent to the sensor for repeat measurements without increasing pressure within the sensor body.

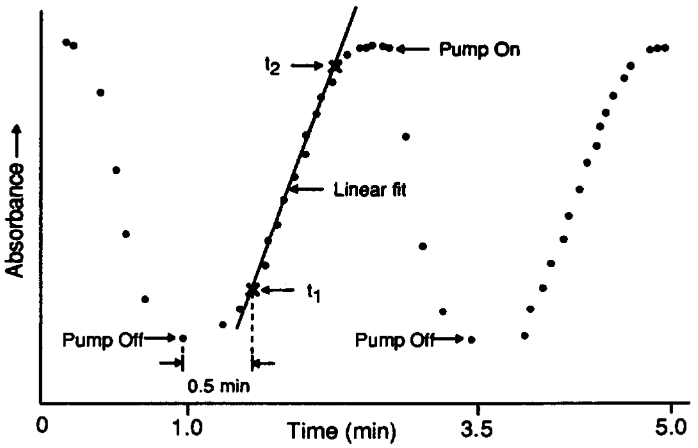


Fig. 5. The sensor is calibrated with consecutive measurements of a known concentration of a target compound and with linear regression. Fresh reagent is delivered at 40 μl/min for 1 min and transmission is measured every 5 sec and converted to absorbance. The slope between t_1 (30 sec after pumping stops) and t_2 (60 sec later) is fit with a linear regression technique. The resulting slope(s) are used to develop a calibration or working curve (as well as determine concentrations of target compounds in field samples). Repeat measurements can be made on demand or at regular intervals of 2.5 min.

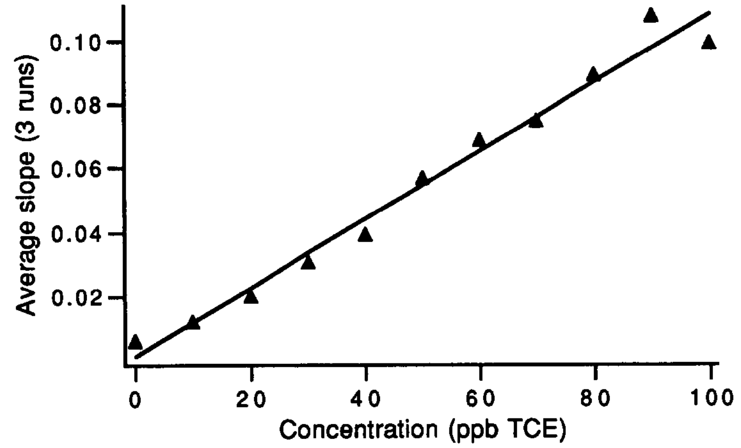


Fig. 6. Calibration or working curve for trichloroethylene (TCE) in water at 0–100 ppb.

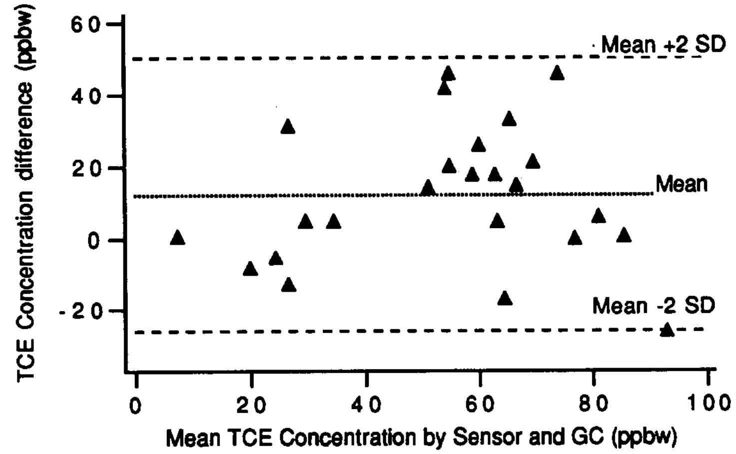


Fig. 7. The mean and deviations of fiber-optic sensor measurements of trichloroethylene (TCE) in groundwater sampled at Lawrence Livermore National Laboratory and gas chromatography (GC) measurements of duplicate samples by an analytical services laboratory. *Y*-Axis is measured GC value minus the fiber optic value.

Table 1. Specificity towards various interfering compounds (response to 1 ppmv)

Compound	Reagent for TCE	Reagent for $CHCl_3$
Tetrachloroethene	none	none
1,1-Dichloroethene	none	none
cis/*trans*-1,2-Dichlorothene	none	none
1,1-Dichloroethane	none	none
1,1,1-Trichlorothane	none	none
Carbontetrachloride	none	minimal*

*Response to 1 ppm CCl_4 was similar to 25 ppb $CHCl_3$

standard dilution). The linear regression for this calibration curve was calculated, and the equation of the resulting line can be used to calculate target molecule concentrations in field samples. Assuming temperature, headspace volume, and liquid volume are known, Henry's constant can be used to convert from liquid to vapor phase concentration and to correct for temperature.

Sensitivity is demonstrated in the calibration or working curve shown in Fig. 6. Here, the same sensor and reagent were used to measure 10 independently prepared test samples of TCE in triple distilled water. The sample concentrations were in 10 increments from 10 to 100 ppbw. The coefficient of correlation to a straight line was $r^2 = 0.989$.

RESULTS AND DISCUSSION

Performance

Fiber-optic sensor measurements were compared with laboratory gas chromatography (GC) of duplicate calibration samples as well as samples from LLNL monitoring wells.[5] In the latter case, 40 monitoring wells containing TCE in a wide variety of concentrations were sampled by an LLNL analytical services contractor. The samples were sent to an analytical services laboratory for GC analysis following US Environmental Protection Agency method 304. We obtained duplicates of each of these samples and immediately measured TCE concentration using the optical sensor. Comparison of the two analytical techniques was made using the statistical method and presentation suggested by Bland and Altman.[6] This method was developed to compare a new measurement technique with an established one. Here, the difference between the GC and fiber-optic sensor analyses is plotted point for point against the average of the two measurement values. Figure 7 displays the result for all wells with concentration below 100 ppbw. Agreement between the two techniques is satisfactory, particularly for a field deployable instrument. The results, however, do indicate that the fiber-optic measurements are generally lower than those of the GC, resulting in a bias of 12 ppbw.

Interferences

Because the Fujiwara reaction is somewhat nonspecific in that it will respond in some degree to other chlorinated hydrocarbons, we have tailored the reagent chemistry to increase the sensor specificity towards TCE. The relative responsiveness of the sensor to several common chlorinated compounds is shown in Table 1.

CONCLUSIONS

The sensor system has been successfully demonstrated in a bench-top configuration as well as in a variety of *in situ* measurements including groundwater and vadose monitoring, pump and treat remediation,[7] and in conjunction with a penetrometer for characterization of soil contamination.[8]

In laboratory tests, the sensor has demonstrated sensitivity to Environmental Protection Agency compliance levels for both TCE and chloroform. Its principal disadvantage is a cross reactivity amongst several halocarbons. This has been reduced to some extent by 'tailoring' the chemical reagents to a particular target compound. This will remain a problem in complex contamination applications; however, many cases have a dominant halocarbon for which the sensor will provide adequate and timely analyses in a variety of application scenarios.

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REFERENCES

1. F. P. Milanovich, P. F. Daley, K. Langry, B. W. Colston, Jr., S. B. Brown and S. M. Angel, A Fiberoptic Sensor for the Continuous Monitoring of Chlorinated Hydrocarbons, in *Proc. 2nd Int. Conf. Field Screening Methods for Hazardous Wastes and Toxic Chemicals*, p. 43. EPA, Las Vegas, 1991.

2. K. Fujiwara, *Sitzungsber. Abh. Naturforsch. Ges. Rostock*, 1916, **6**, 33.
3. S. M. Angel, P. F. Daley, K. C. Langry, R. Albert, T. J. Kulp and I. Camins, *The Feasibility of Using Fiber Optics for Monitoring Groundwater Contaminants VI, Mechanistic Evaluation of the Fujiwara Reaction for the Detection of Organic Chlorides.* Lawrence Livermore National Laboratory, Livermore, CA, UCID-19774, 1987.
4. R. J. Berman, G. C. Christian and L. W. Burgess, *Anal. Chem.*, 1990, **2**, 2066.
5. F. P. Milanovich, S. B. Brown, B. W. Colston, Jr., and P. F. Daley, *A New Fiber-Optic Sensor Technology for Rapid and Inexpensive Characterization of Soil Contamination.* Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-113731, 1993.
6. J. M. Bland and D. G. Altman, *Lancet*, 1986, **8476**, 307.
7. B. W. Colston, Jr., S. B. Brown, P. F. Daley, K. Langry and F. P. Milanovich, Monitoring Remediation of Trichloroethylene Using a Chemical Fiber Optic Sensor: Field Studies, in *Proc. Int. Topical Meet. Nuclear and Hazardous Waste Management*, Vol. 1, p. 393. American Nuclear Society, Inc., La Grange Park, Illinois, 1992.
8. F. P. Milanovich, S. B. Brown, B. W. Colston, Jr., and P. F. Daley, A New Fiber-Optic Sensor Technology for Rapid and Inexpensive Characterization of Soil Contamination, in *Contaminated Soil '93 Proc.*, Vol. II, p. 1633. Kluwer Academic, Germany, 1993.