A FiberOptic Sensor for the Continuous Monitoring of Chlorinated Hydrocarbons

F.P. Milanovich[1], P.F. Daley[2], K. Langry[1], B.W. Colston[1] Jr.,
S.B. Brown[1], and S.M. Angel[1]
[1]Environmental Sciences Division,
[2]Environmental Restoration Division
Lawrence Livermore National Laboratory
Livermore, CA 94550

Abstract

We have developed a fiber optic chemical sensor for use in groundwater and vadose zone monitoring. The sensor is a result of modification of previous work in which we demonstrated a fluorescence based sensor for the non-specific determination of various volatile hydrocarbons. The principle of detection is a quantitative, irreversible chemical reaction that forms visible light absorbing products. Modifications in the measurement scheme have lowered the detection limits significantly for several priority pollutants. The sensor has been evaluated against gas chromatographic standard measurements and has demonstrated accuracy and sensitivity sufficient for the environmental monitoring of trace levels of the contaminants trichloroethylene (TCE) and chloroform.

In this paper we describe the principles of the existing single measurement sensor technology and show field test results. We also present the design of a sensor which is intended for continuous, sustained measurements and give preliminary results of this sensor in laboratory experiments.

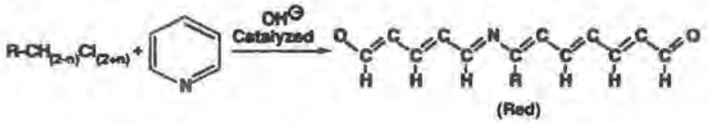
Background

This sensor technology is an outgrowth of research initially sponsored by the U.S. Environmental Protection Agency. Here, a fluorescence based probe for the remote detection of chloroform was conceived, developed and demonstrated in the mid-1980's.[1] The sensitivity and accuracy of the probe proved insufficient for many monitoring applications and research was discontinued. However, in DOE sponsored research one of us (SMA) invented a new concept sensor that has demonstrated significantly improved sensitivity and accuracy for both TCE and chloroform.[2] This sensor is currently under evaluation in monitoring well and vadose zone applications.

Principles of Operation

The basic components of the sensor technology are the chemical reagent, electro-optic measurement device, and the sensors. For the latter, we have developed two versions, one for single and one for continuous measurements. A brief desrciption of the components follows.

Chemistry. The chemical basis of this technology is the irreversible development of color in specific reagents upon their exposure to various target molecules. The primary reagent is an outgrowth of the work of Fujiwara[3] who first demonstrated that basic pyridine,when exposed to certain chlorinated compounds, developed an intense red color. This red color is due to the formation of highly conjugated molecules as shown below. We and others have since demonstrated that this and closely related reactions can be used to detect trace amounts of these same compounds.[4]



Sensors The single measurement sensor (Fig 1) is comprised of the terminus of two optical fibers and an aliquot (20 µl) of reagent in a small capillary tube. The fibers are sealed into one end of the capillary tube and reagent is placed into this capillary to a length of approximately 5 mm. A porous teflon membrane is placed over the open end of the capillary to prevent loss of the reagent. Target molecules, TCE for example, readily pass through the membrane and produce color in the reagent. This color results in decreased transmission of light at 540 nm. The measurement of the time history of the color development provides a quantitative measure of the target molecule concentration. Since the reaction is non-reversible, the reagent must be replenished for every measurement. This is readily accomplished through the use of easily replaceable, disposable capillaries.

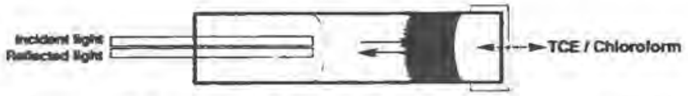


Figure 1. Schematic of the single-measurement sensor

Figure 2 shows a sensor that has been designed for continuous operation.[5] It is essentially identical to the single measurement version with the exception of the addition of two micro-capillary tubes. These are used to supply new reagent to the sensor either continuously or on demand.

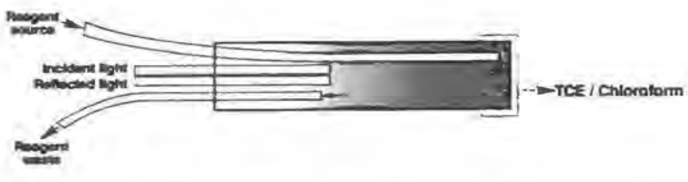


Figure 2. Schematic of the continuous-measurement sensor

Electro-optics. The readout device is shown highly schematically in Fig 3. Here the emission of a miniature tungsten-halogen lamp is collected by suitable optics, chopped with a tuning fork and directed into an optical fiber. The fiber transmits this light with high efficiency to the sensor where it passes through the chemical reagent, reflects off the teflon membrane, and is collected by a second optical fiber. This latter fiber transmits the reflected light to an optical block where it is divided into two beams by a long pass dichroic mirror. These resulting beams are optically filtered at 540 nm and 640 nm, respectively, and their intensity is ultimately measured with silicon photodiodes using phase sensitive detection techniques.

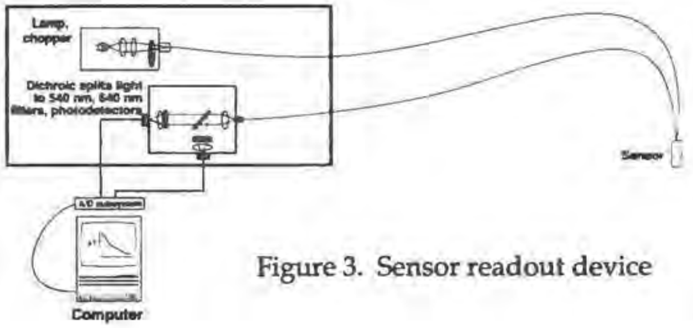


Figure 3. Sensor readout device

Since the colored product absorbs strongly at 540 nm and is virtually transparent at 640 nm, the ratio of 540 to 640 gives a nearly drift free measure of 540 nm absorption. The sensors are calibrated in two ways (1) in the headspace above standard TCE solutions of known w/w concentration or (2) in vapor phase using calibrated dilutions (v/v) of dry TCE vapor. Figure 4 shows the time dependent transmission of sensors exposed to TCE standard solutions and a resulting calibration curve.

Results and Discussion

Groundwater monitoring. The sensor has been evaluated against contractor sample and analysis of 40 monitoring wells located within the boundary of LLNL. These wells are sampled quarterly with subsequent chemical analysis performed by EPA standard 624 purge and trap gas chromatography (GC). We obtained concurrent samples during the quarterly contractor sampling and used our fiber sensor to make

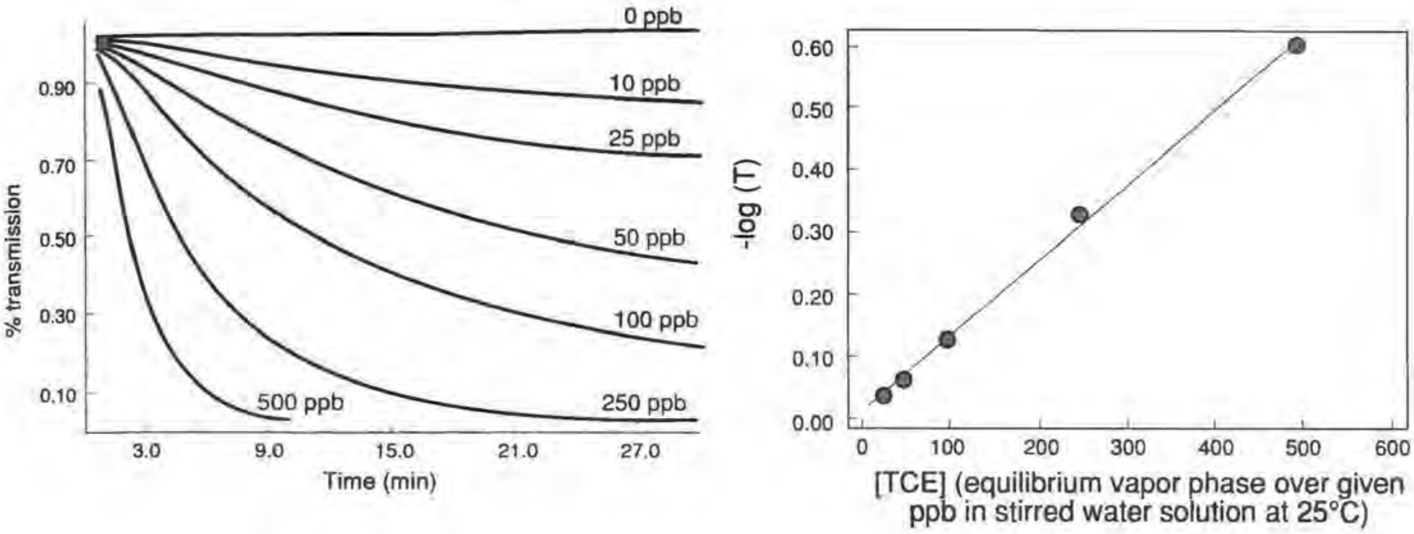


Figure 4. Sample transmission ratio curve, and working standard curve for dual-wavelength absorption sensor. Standard curve obtained from % transmission at a fixed time following iniation of exposure

duplicate TCE concentration determinations. Figure 5 shows a diagram of the laboratory measurement apparatus. Samples were sequestered with no head space into 250 ml Pyrex bottles. These were immediately returned to the laboratory and divided in half. The fiber sensor was then introduced into the resulting headspace through a gas tight valve and a measurement was initiated after stirring the sample for 5 minutes.

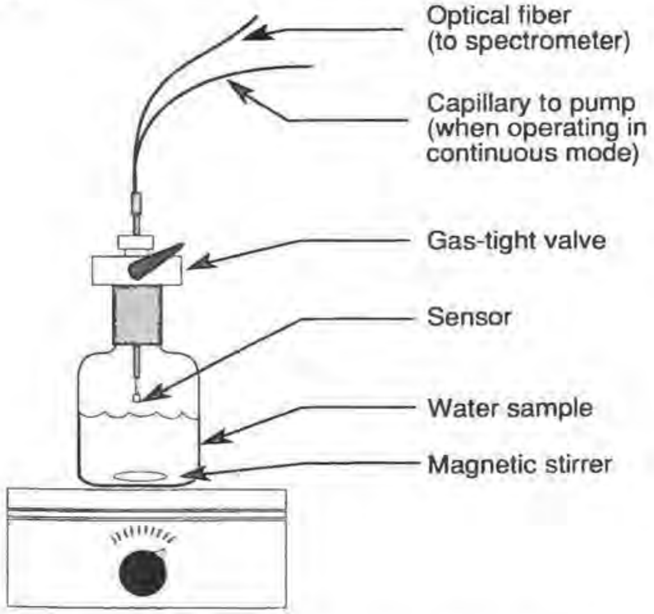


Figure 5. Schematic of vessel used for laboratory headspace measurements

Table 1 below shows the comparison of some of the contractor measurements with the fiber sensor. All fiber sensor values are the average of the duplicate samples. There is excellent agreement between the GC and fiber sensor determinations with nearly all values within the variance of the GC.

Vadose zone monitoring. LLNL site 300 was chosen as the location for initial vadose zone evaluation of the fiber sensor. The vadose zone was accesssed at several locations through existing dedicated soil vapor monitoring points. The samples were drawn at nominally 450 cc/min through copper tubing to a remote mobile laboratory. The lab contained both the fiber sensor apparatus and a portable GC. The instruments were connected to the sample stream in series as depicted in Fig 6 below. Both devices were calibrated for TCE

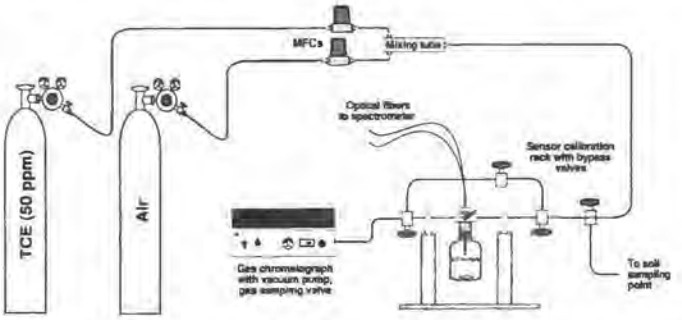


Figure 6. Schematic of vadose zone sampling and calibration apparatus. Sample air is drawn with a pump on board the GC

Table 1. Representative data from field calibration study, compiled from TCE measurements from monitoring wells and piezometers at LLNL.

		[TCE](ppb)				[TCE](ppb)	
Well	Date	Fiber	GC	Well	Date	Fiber	GC
MW352	2/13/90	44	58	MW357	2/13/90	78	84
P418	2/13/90	54	72	P419	2/13/90	61	66
MW271	3/7/90	86	160	MW364	3/7/90	59	74
MW217	3/5/90	106	86	MW458	3/6/90	33	20
MW365	3/6/90	27	22	MW142	3/6/90	94	140

measurements with precision gas mixtures prior to sampling. The fiber sensor tracked the GC very well through a wide range of concentrations. Figure 7 is a particularly interesting result. Here both instruments were compared in a nearly contamination free location. It is clear that the GC was at its limit of detection, whereas the fiber sensor readily made a successful measurement. Estimates of TCE concentration for this location was <10 ppb.

Continuous measuring sensor. The above described sensor has demonstrated adequate sensitivity and accuracy to represent a viable new environmental monitoring technology. However, the current design,

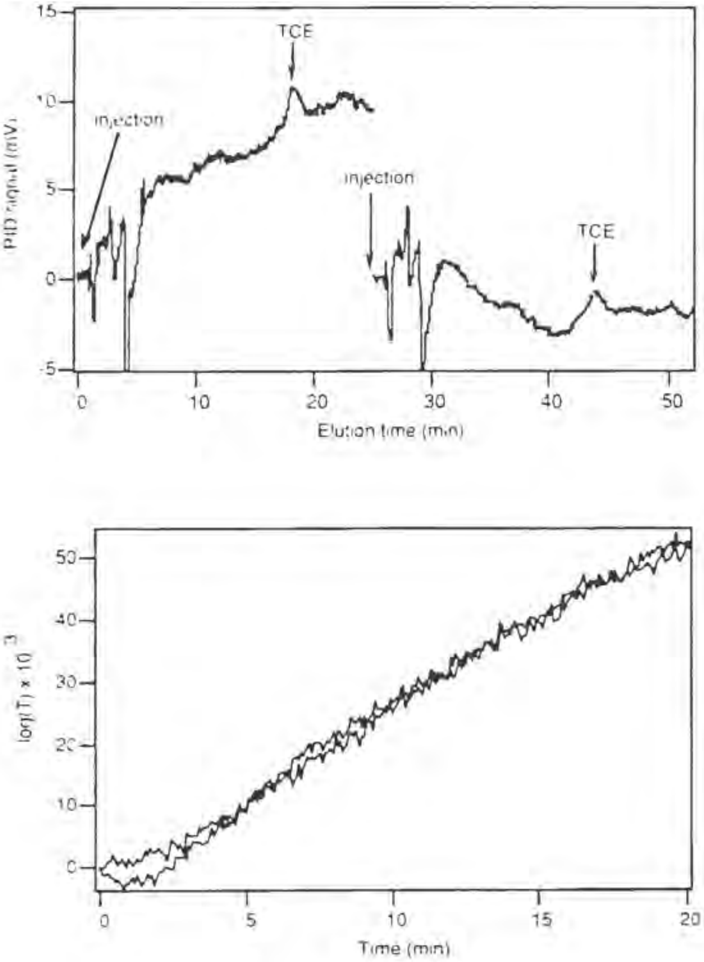


Figure 7. Results of (above) GC (SRI Instruments 8610, PID detector, 6' x 1/8" silica gel column), and (below) fiber sensor measurement of extremely low TCE levels in soil gas (estimated to be ~150 ppb$_v$, i.e.: 150 μmoles TCE per mole air).

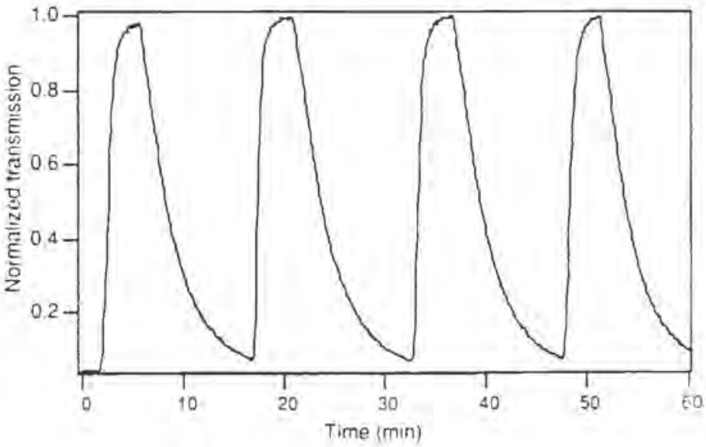


Figure 8. On-demand measurement of 10 ppm TCE (i.e.: headspace measurement over water containing 10 ppm TCE) with continuous sensor system

which incorporates an irreversible chemical reaction, requires the sensor to be refurbished subsequent to each measurement. This liability limits its application somewhat in environmental monitoring.

The sensor shown in figure 2 represents the lowest risk mitigation of this liability. Preliminary reslts with prototypes of this sensor are very promising. Figure 8 shows typical on-demand measurements obtained with this sensor in laboratory testing. We anticipate that this sensor will become an integral component in a down-well monitoring instrument currently being developed at LLNL.

Acknowledgements

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