

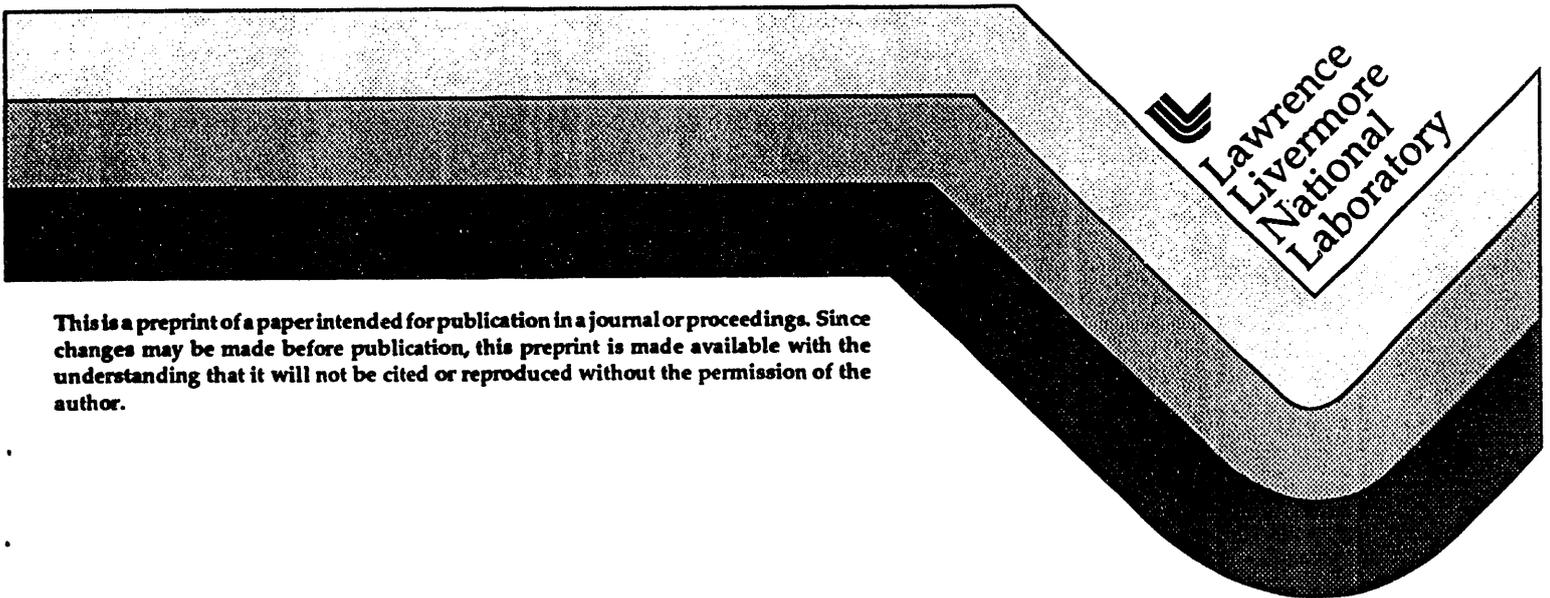
UCRL-JC-112182  
PREPRINT

**Penetrometer Compatible, Fiber-Optic Sensor for  
Continuous Monitoring of Chlorinated Hydrocarbons-  
Field Test Results**

**F. P. Milanovich, S. B. Brown, and B. W. Colston Jr.**

**This paper was prepared for submittal to the  
Chemical Sensors Symposium  
May 16-21, 1993  
Honolulu, Hawaii**

**April 1993**



**This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.**

**MASTER**

**DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED**

*CVP*

### **DISCLAIMER**

**This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.**

# Penetrometer Compatible, Fiber Optic Sensor for Continuous Monitoring of Chlorinated Hydrocarbons - Field Test Results

Fred P. Milanovich, Steve B. Brown,  
and Billy W. Colston Jr.

Environmental Science Division  
Lawrence Livermore National Laboratory  
Livermore, CA 94550

## Abstract

We have developed and field tested a fiber optic chemical sensor for use in environmental monitoring and remediation<sup>1</sup>. The principle of detection is colorimetric and is based on an irreversible chemical reaction<sup>2</sup> between a specific reagent and the target compound. The formation of reaction products are monitored remotely with optical fibers. Successive or on-demand measurements are made possible with a reagent reservoir and a miniature pumping system. The sensor has been evaluated against gas chromatography standards and has demonstrated accuracy and sensitivity (>5ppb w/w) sufficient for the environmental monitoring of the contaminants trichloroethylene (TCE) and chloroform. The sensor system can be used for bench-top analyses or for in-situ measurements such as groundwater and vadose monitoring wells or in Penetrometry mediated placements.

## Experimental

The primary chemical reagent used in the sensor is an outgrowth of the work of Fujiwara<sup>2</sup>, 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 that exhibit strong absorption in the blue-green region of the spectrum. Some selectivity of target molecules is possible through modifications of the reagents and their relative concentrations<sup>3</sup>.

The reagent used to detect trichloroethylene(TCE), for example, is a mixture of 99% pyridine (by volume) and 1% tetrabutylammonium hydroxide(TBAH, 40% aqueous solution by weight). In the presence of the base, TCE reacts with the pyridine and forms a colored product. The reaction only requires very dilute amounts of the analyte to proceed, so sensitivity of the sensor is excellent. The reagent is highly stable over time and can be stored and used for several weeks to months.

A benchtop version of the measurement system is shown schematically in Fig. 1 below. Its basic components are a pumping system, which consists of a

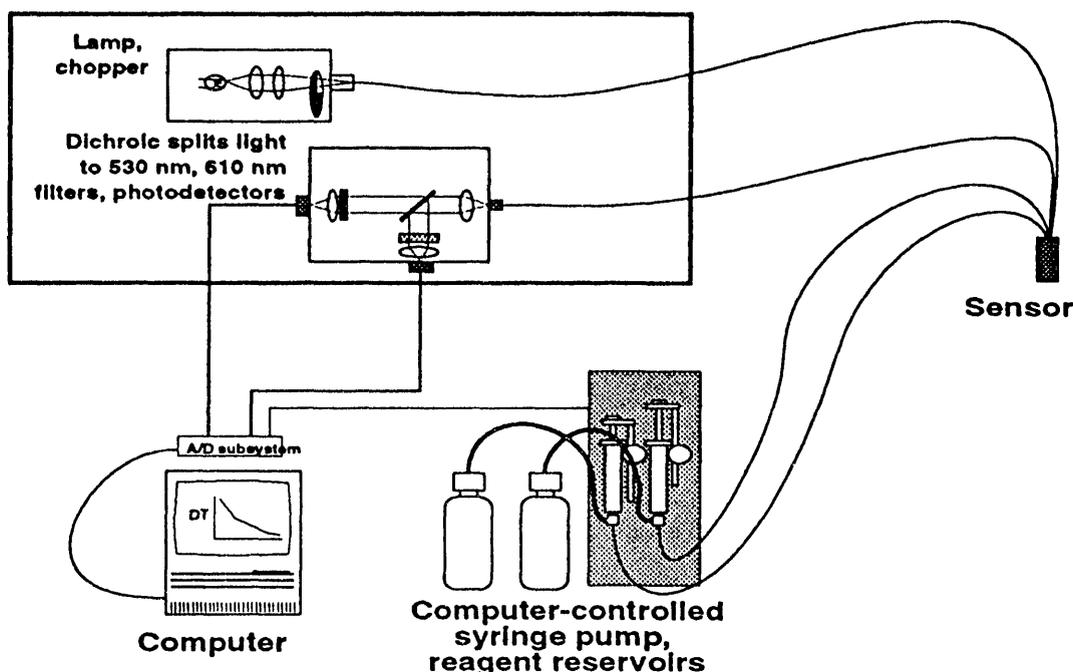


Figure 1 (a) Schematic of measurement system

computer controlled syringe pump and six-way valve, for renewing the chemical reagent; an electro-optic read-out device, consisting of an incandescent lamp, suitable filters and silicon diode detectors, for measuring sensor transmission; and the sensor itself. The principal components of this system have been miniaturized to fit within a penetrometer cone (essentially a 1.25" i.d. pipe).

The sensor, Fig. 2, allows consecutive measurements to be taken at short intervals on an on-demand basis, with control and monitoring being executed remotely. The cell consists of a semipermeable, flexible tube connected at both ends by stainless steel capillaries. One capillary contains the input fiber and fill tube while the other contains the output fiber and a drain tube. The components are potted in the capillaries using epoxy. A thermocouple is placed in the middle of the loop so vapor temperature can be continuously monitored.

Target molecules, TCE for example, diffuse through the semipermeable membrane of the exposed tubing and react with the reagent inside. In the presence of TCE the reagent absorbs light in the green region of the spectrum

(530-570nm). This absorbance, which is recorded against time, provides a direct measure of TCE vapor concentration.

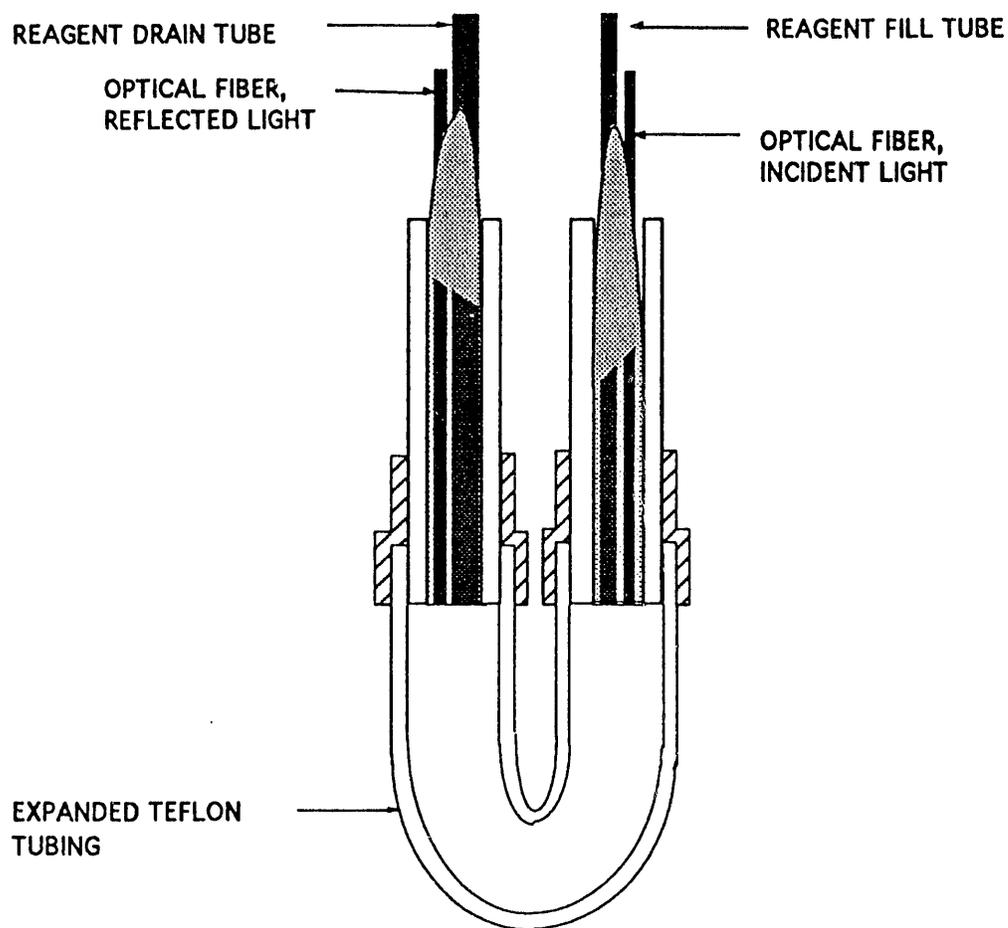


Figure 2. Schematic of on-demand sensor

The sensor has been evaluated against gas chromatography standards and has demonstrated accuracy and sensitivity (<5ppb w/w) sufficient for the environmental monitoring of the contaminants trichloroethylene (TCE) and chloroform. The sensor system can be used for bench-top analyses or for in-situ measurements such as groundwater and vadose monitoring wells or in Penetrometry mediated placements. The sensor has been successfully used to monitor TCE in 2 and 4 inch diameter monitoring wells, in a soil vapor remediation feed line, and has demonstrated a 48 hour consecutive measurement during an aquifer flow test

## Results and Discussion

The objectives of the work reported here were to deliver the sensor, using cone penetrometry, to multiple depths at multiple locations, to expose the sensor to a range of TCE concentrations, and to observe the effect that pumping, as in a vadose zone 'grab sample' operation, has on the measurement process.

A custom penetrometer cone was designed by S. Cooper of the U. S. Army Corps of Engineers Waterways Experiment Station (COE/WES) and S. Brown of Lawrence Livermore National Laboratory (LLNL) and was constructed at LLNL. The cone (495 mm long, 44.5 mm o. d., 33.75 mm i.d.) is threaded to receive standard 1 m  $\times$  33.75 mm COE/WES push rods. The reagent delivery system and sensor are housed in the cone and are isolated from the environment until the measurement depth is reached. The TCE sensor was exposed to soil vapors by means of a removable and disposable ground-penetrating tip. The cone is driven to the desired depth and then retracted by 15 cm, thereby leaving the removable tip at depth while exposing the sensor to soil vapors and creating a void or "probed volume" of approximately 200 mm<sup>3</sup>. Communication from the ground surface to the sensor and support equipment housed in the cone is accomplished with a custom-built 60 m long umbilical cord containing two optical fibers, a tube for vacuum evacuation of the probed volume, and a six-wire electrical cable for electronic instruction delivery and data acquisition.

Four separate pushes (to depths of 9, 14, 41 and 33 meters) were accomplished over two days. Measurements were made in both a quiescent ("static") and vacuum extraction ("dynamic") mode. A total of 121 individual TCE concentration measurements were made during the four pushes; measured concentrations ranged from ~2 ppm by volume (static measurement at 9 m depth) to ~120 ppm by volume (dynamic measurement at 14 m). It is of particular note that the time to depth for the 41 m push was only 50 min.

Table 1 gives the results of an extended experiment performed after the sensor was pushed to 33 m, which placed it approximately 6 m above the water table. We made three measurements with the cone tip in place to zero the sensor and then removed the tip and made 15 consecutive static measurements. The TCE concentration was  $18.8 \pm 5.0$  ppm. We then performed nine consecutive measurements under dynamic conditions. Here the concentration jumped abruptly into the 30-ppm range and remained stable for the duration of pumping, yielding a TCE concentration of  $34 \pm 1.3$  ppm. When we discontinued pumping, the concentration almost immediately dropped back to the previous static values (average concentration  $14.4 \pm 1.8$ ). This is slightly less than the initial measurements but identical within experimental uncertainty. It is noteworthy that the first three measurements after retraction of the tip gave higher results than the next eight measurements. This is probably attributable to the vacuum, and the resulting greater soil extraction, generated upon initial retraction of the cone to form the probed volume. Removing the first three measurements (29.8, 26.9 and 20.0 ppm) from the initial static set yields a mean TCE concentration of  $16.1 \pm 1.4$  ppm, which agrees very well with the mean and uncertainty obtained

during the second static set of measurements. One possible explanation for the higher values obtained during pumping is increased volatility of the TCE during flowing conditions.

TABLE 1. Measured TCE concentrations under static (unpumped) and dynamic (vapor extraction) conditions.

Pump	[TCE] (ppm, by volume)											Average	
Off	29.8	26.9	20.2	18.2	18.0	16.6	16.7	15.8	15.2	15.0	14.6	14.6	18.8
On	35.2	33.7	32.1	33.6	33.3	32.5	36.2	35.2	34.3	34.3	34.3	34.3	34.0
Off	23.7	18.4	16.0	15.5	14.2	13.2	14.4	12.9	13.0	13.0	13.2	13.2	14.4

### Conclusions

All objectives of this initial penetrometer-mediated sensor-placement demonstration were accomplished. This technology represents the most rapid and cost-effective means to obtain initial survey information on subsurface contamination distribution for a variety of chlorinated solvents. Its impact on optimizing the siting of monitoring wells will significantly reduce remediation costs.

This work is supported by the DOE Office of Technology Development and performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48. We are indebted to Dr. Lloyd Burgess and the Center for Process Analytical Chemistry, University of Washington, for collaboration that led to the design and demonstration of the continuous sensor. We acknowledge the invaluable contributions of the COE/WES staff and Dr. Joe Rossabi of the Savannah River Company during the course of the field experiments.

### References

1. B. W. Colston, Jr., S. B. Brown, P. F. Daley, K. Langry, and F. P. Milanovich (1992, August), "Monitoring Remediation of Trichloroethylene Using a Chemical Fiber Optic Sensor: Field Studies," *Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management*, Vol. 1, 393-396.
2. K. Fujiwara (1916), *Sitzungsber. Abh. Naturforsch. Ges. Rostock* 6, 33.
3. S. M. Angel, P. Daley, K. Langry, R. Albert, T. Kulp, and I. Camins (1987, Jun), *Mechanistic Evaluation of the Fujiwara Reaction for the detection of Organic Chlorides*, Lawrence Livermore National Laboratory, Livermore, CA, UCID-19774.

**END**

---

**DATE  
FILMED**

**10/01/93**

