

Demonstration of a VOC *In-Situ* Fiber Optic Sensor for Use With a Penetrometer Analysis System

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ABSTRACT

Researchers at the Idaho National Engineering Laboratory with their industrial CRADA partner GEO-CENTERS demonstrated a fiber optic based VOC sensor at the Army Environmental Center (AEC) technology demonstration at Dover Air Force Base. The sensor used during the demonstration was a single fiber optic cable coupled to an *in situ* sensor element contained in a cone penetrometer tip. The sensor's fluorescence response was measured at the surface using an optical breadboard-based instrument. Results from this demonstration showed that the sensor provided semi-quantitative results for total VOCs comparable to the historical values of VOCs. In addition, the demonstration identified several technical challenges for improvement of the sensor. This paper describes the analytical properties of the reversible sensing materials, construction of an improved sensor system, and the planned demonstration of the modified *in-situ* VOC sensor system. This sensor system is tentatively scheduled for demonstration at the Army Environmental Center's Aberdeen Proving Ground Test site. Improvements to the VOC sensor system include an optical configuration that will correct for soil matrix interferences and multiple sensing substrates to learn whether VOC selectivity can be achieved.

KEYWORDS: VOC, optical probe, fluorescence, field screening, cone penetrometer

1. DESCRIPTION OF VAPOCHROMIC RESPONSE

There are many chemical specific, colorimetric compounds designed to provide a measurable response to volatile organic compounds (VOCs). However, none of these sensors incorporate the desired combined properties of stability, selectivity, sensitivity, and reversibility needed for a rapid hand-held instrument for identifying and quantifying VOCs at regulatory levels.

Developments of patented compounds by the 3M Corporation<sup>1,2</sup> have resulted in the manufacture of vapo-chromic VOC indicators (Figure 1) which typically show a rapid and reversible shift in their absorbance (vapo-chromism) or emission spectra upon inclusion of VOCs.<sup>3</sup> Research at the INEL has demonstrated that these materials have the potential to be used in inexpensive, portable, optical VOC detection systems.

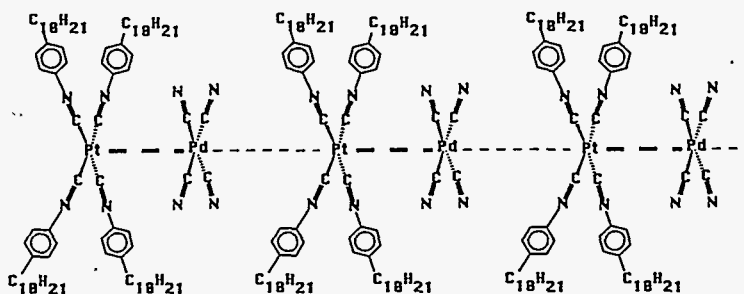


Figure 1. Model of C<sub>10</sub>-Pt/Pd stacked salt complex.

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For this research, “vapochromes” are  $[\text{Pt}(\text{aryl isonitrile})_4][\text{Pd}(\text{CN})_4]$ -based compounds (where aryl isonitrile =  $p\text{-CN-C}_6\text{H}_4\text{-C}_n\text{H}_{2n+1}$ ;  $n=6,10,12,14$ ). These compounds are stacked structures of Pt-dications and Pd-dianions that form brightly colored insoluble salts. The  $\text{C}_{10}\text{-Pt/Pd}$  salt changes color rapidly and reversibly from pink to blue when exposed to selected volatile organic compounds. An example of this color change can be seen by monitoring the absorbance spectra of the  $\text{C}_{10}\text{-Pt/Pd}$  as it is exposed to chloroform vapors (Figure 2). The magnitude of the shift is determined by the concentration and identity of the volatile. Further investigation of these spectral observations also showed that the vapochromes produce a fluorescence which can spectrally shift upon exposure to various VOCs. Again, the magnitude of the shift is dependent upon the excitation wavelength and the volatile organic compound. Table 1 lists the absorbance and fluorescence spectral shifts for the  $\text{C}_{10}\text{-Pt/Pd}$  compound as it is exposed to different VOCs. Substitutions to the functional groups or metal-metal structure have yielded spectrally different compounds with similar VOC responsive behavior.

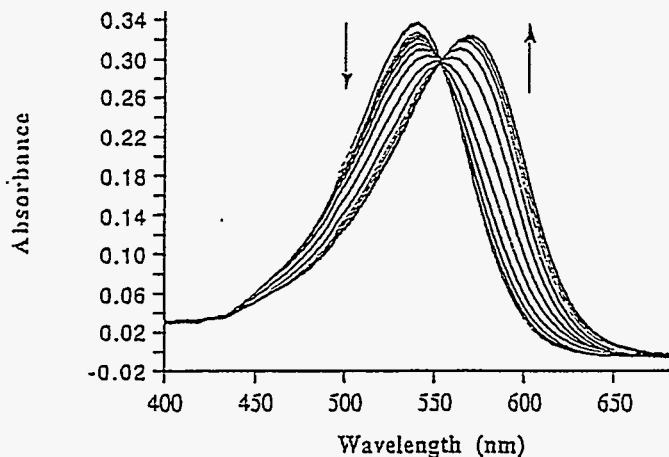


Figure 2. Absorbance of  $\text{C}_{10}\text{-Pt/Pd}$  as exposed to chloroform.

Table 1. Absorption and Emission  $\lambda_{\text{max}}$  for VOC exposed films of  $[\text{Pt}(p\text{-CN-C}_6\text{H}_4\text{-C}_{10}\text{H}_{21})_4][\text{Pd}(\text{CN})_4]$ .

Solvent	Absorption	Vapochromic Shift <sup>a</sup>	Emission Maximum <sup>b</sup>	Vapochromic Shift
none	548	---	640	---
MeOH	544	-4	621	-19
2-PrOH	554	6	c	c
Et <sub>2</sub> O	558	10	c	c
CH <sub>3</sub> CN	559	11	642	2
hexanes	561	13	640	0
acetone	562	14	650	10
benzene	567	19	642	2
CH <sub>2</sub> Cl <sub>2</sub>	569	21	653	13
CHCl <sub>3</sub>	578	30	658	18

<sup>a</sup> Vapochromic shift is  $\lambda_{\text{max}}(\text{VOC}) - \lambda_{\text{max}}(\text{none})$ .

<sup>b</sup> Films were excited at the isobestic points determined from vapochromic absorption data.

<sup>c</sup> No data collected.

## 2. ADSORPTION STUDIES OF VAPOCHROME

Research of the vapochromes' analytical response characteristics began with a fundamental evaluation of the VOC adsorption capabilities. These adsorption capabilities will ultimately establish the limits for sensor sensitivity, response time, linearity, selectivity, and reproducibility. To determine these adsorption characteristics, a mass absorption sensing device, the quartz crystal microbalance (QCM) was used to observe the amount and rate at which VOCs are adsorbed onto the vapochromes. The QCM system (Figure 3) was constructed to measure the mass change that occurs when a quartz crystal, coated with a vapochrome C<sub>10</sub>-Pt/Pd selectively adsorbs VOCs from air. Because the QCM can detect nanogram to microgram mass changes on the quartz crystal, the QCM system can detect VOC interactions with the vapochromes at low gas concentrations. The QCM system consisted of series of flow control valves, contaminant scrubbing traps, a temperature and humidity recorder and a referencing QCM crystal.

For the QCM experiments, the quartz crystals were coated with 20 to 100 micrograms of vapochrome. The coatings were deposited from a reservoir containing a dispersion of methylene chloride, hexane, and vapochrome onto the crystals with an air brush. Once loaded into the detection cell, the vapochrome response was observed by alternating the flow of pure air and VOC spiked air (Figure 4) over the crystal. With this technique, the ability of the vapochrome to reversibly and reproducibly detect VOCs was observed. Also, the response showed that the vapochrome begins to measurably absorb VOCs within seconds and then can return reversibly to baseline response within two minutes of exposure to clean air.

In addition to the response time, the C<sub>10</sub>-Pt/Pd material was found to selectively adsorb linearly short-chain chlorinated hydrocarbons, light aromatics, and some alcohols at 2 ppm. Specific compounds that produced a response included carbon tetrachloride, chloroform, methylene chloride, trichloroethylene (TCE), trichloroethane, benzene, toluene, and xylene (BTEX) (Figure 5). The vapochrome did not adsorb short chain hydrocarbons like methane or butane or inorganic gases such as CO, CO<sub>2</sub>, HCN, H<sub>2</sub>S, or NO<sub>x</sub>.

Overall, the vapochrome when evaluated using the QCM as a sensor transducer is: 1) linear over two orders of magnitude; 2) reproducible within <10% relative standard deviation for replicates; 3) accurate within 5 to 50% of known concentrations; 4) rapid, reaching 80% of maximum response within 60 s; and 5) reversible, returning to 5% of baseline within 120 s. This combination of these capabilities indicate that vapochromes have the potential to be good spectral indicator for VOCs.

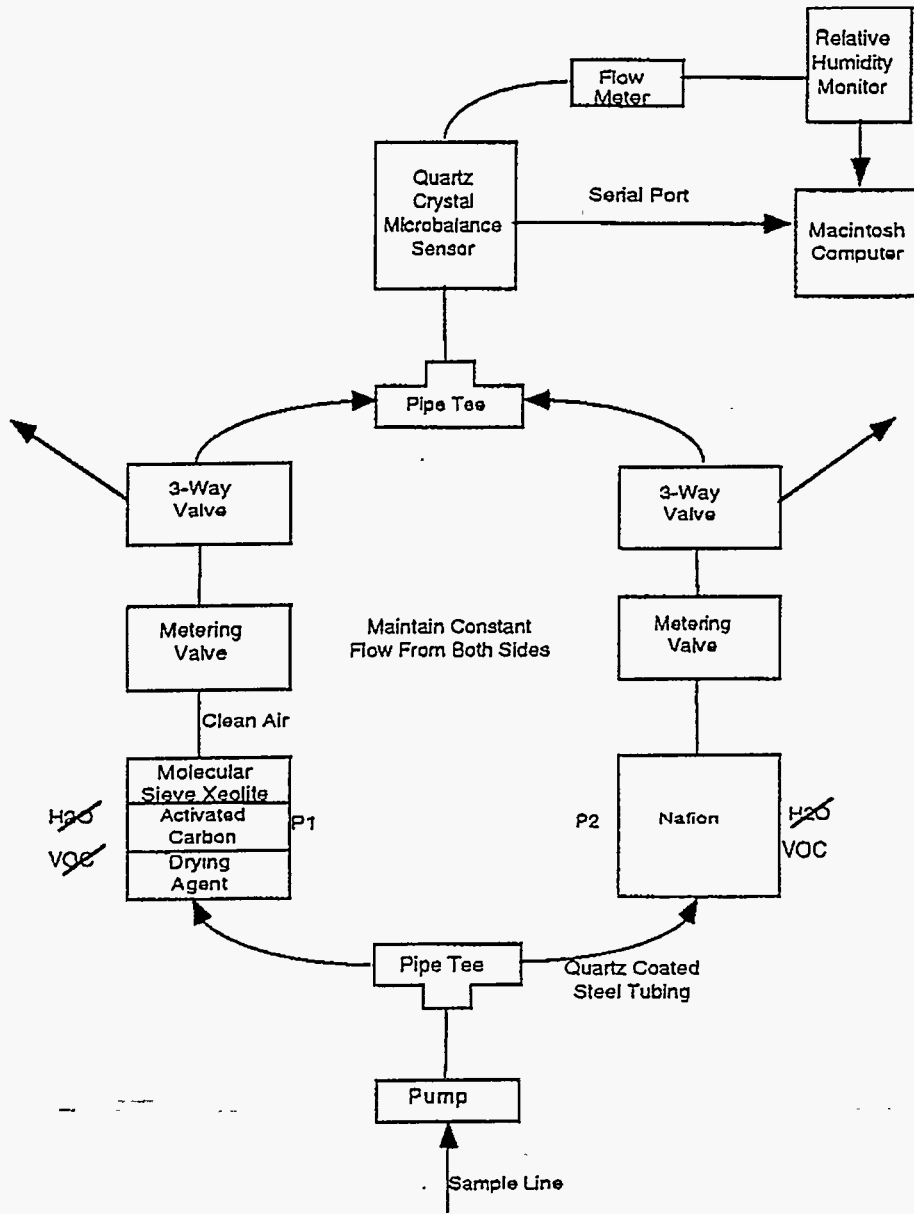


Figure 3. Schematic of QCM sensor system.

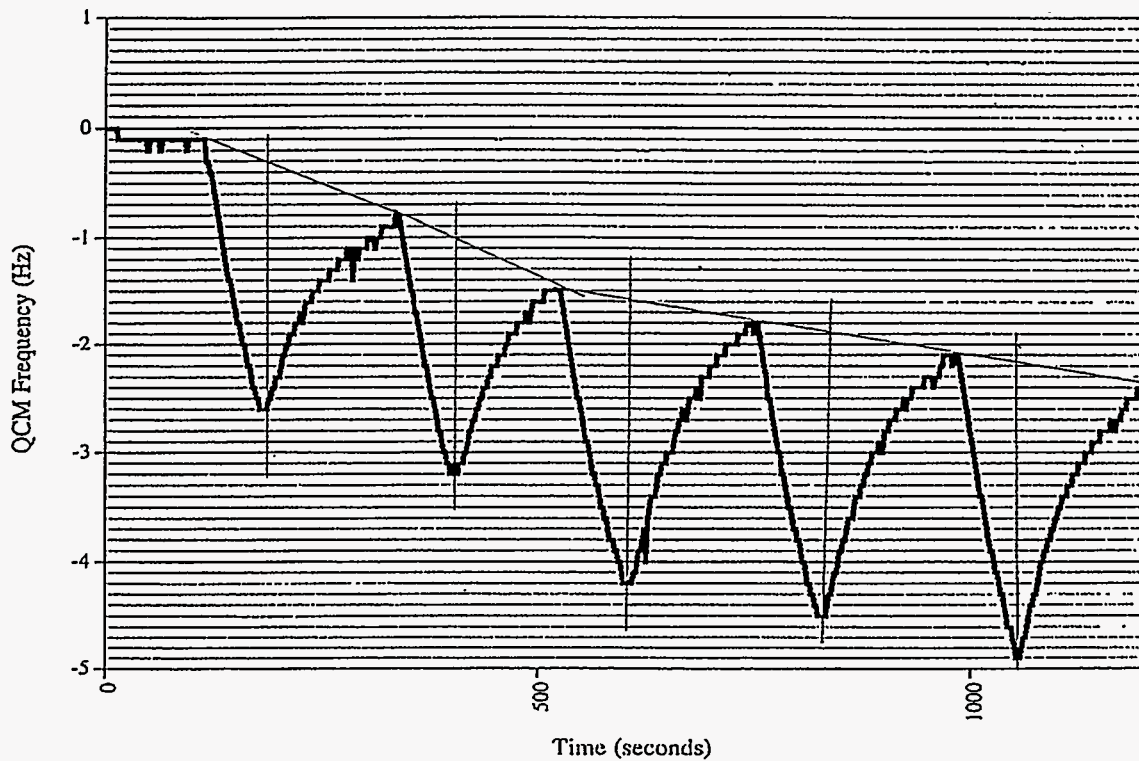


Figure 4. QCM system data for  $C_{10}$ -Pt/Pd coated crystal exposed repeatedly to 15 ppm chloroform.

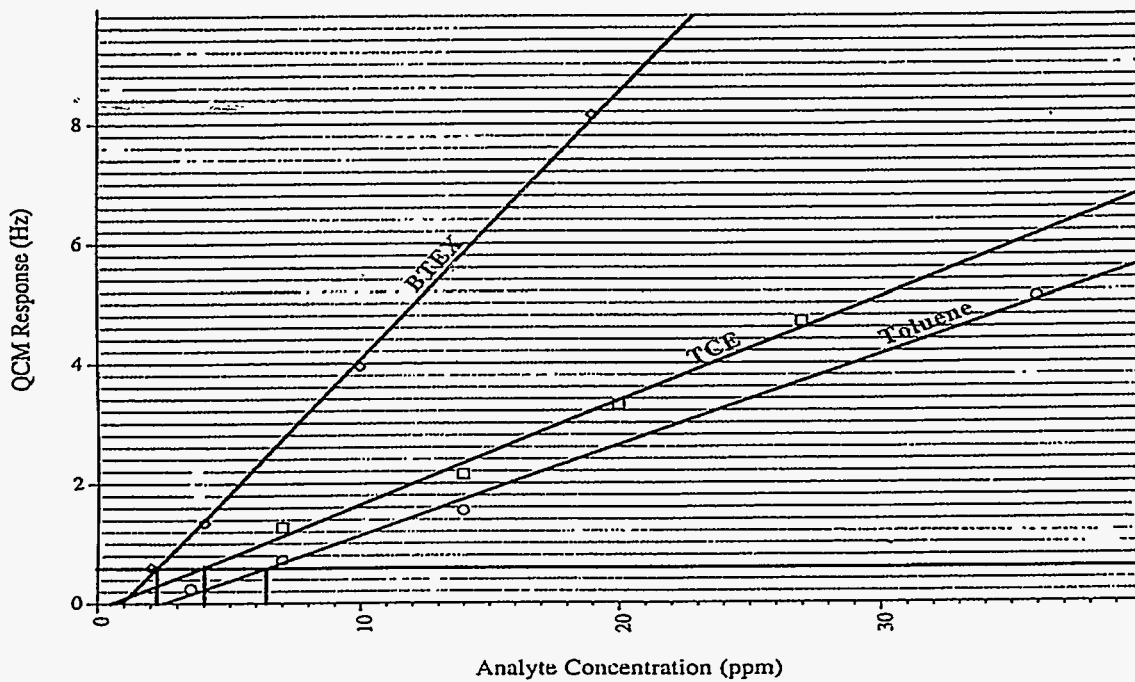


Figure 5. QCM system data output for quartz crystal coated with  $C_{10}$ -Pt/Pd when exposed to various concentrations of VOCs.

### 3. DEMONSTRATION OF FLUORESCENCE DETECTION SYSTEM AT DOVER AIR FORCE BASE

The Army Environmental Center (AEC) sponsored a technology demonstration at Dover Air Force Base, Dover, DE, on May 8-26 1995. The purpose of the demonstration was to evaluate several VOC sensors and field-deployable analytical instruments being developed with AEC funding. During this demonstration, the INEL and industrial cooperative research and development agreement partner GEO-CENTERS Inc. (Newton Center, MA) evaluated a laboratory prototype fiber optic-based vapochromic VOC sensor. Test objectives for the demonstration of the GEO-CENTERS/INEL sensor were as follows: 1) configure a robust and reversible VOC sensor for use with the AEC's Site Characterization Analysis Penetrometer System (SCAPS), 2) qualitatively detect 100 to 10000 ppm VOC vapors in the vadose zone using SCAPS, and 3) evaluate sensor performance and define technology development needs.

The sensor consisted of a single fiber optic cable coupled to an *in situ* cone penetrometer sensor element (Figure 6). The sensor element contained C<sub>10</sub>-Pt/Pd vapochrome dispersed in a polymeric coating deposited on the surface of small glass beads. The vapochrome's fluorescence response was transported from the penetrometer via an optical fiber to the surface and evaluated with an optical breadboard-based instrument loaned to GEO-CENTERS by Rutgers University (Figure 7). The optical response was recorded as changes in the vapochrome's fluorescence emission at 610 nm (80 nm full width half maximum bandwidth), excited with a 475 nm (60 nm full width half maximum bandwidth) light source. As the penetrometer was pushed through the soil, vadose zone gases were drawn into the cone penetrometer sensor detection cell via a vacuum pump operated from the surface. Baseline responses were reestablished by pumping ambient air from the surface into the detection cell.

The demonstration site was near a building on the base in which turbine engines are overhauled. Previously, substantial quantities of chlorinated hydrocarbons, (e.g., trichloroethylene and tetrachloroethylene) used to clean engine components, had leaked into the vadose zone (at 4 to 9 ft) and the water table (at 9.5 ft). Characterization of the vadose zone in this area has established that VOC contamination of 100 to 2000 ppm in both sand and clay layers. Over the two days of testing for the sensor, three penetrometer pushes were made, one the first day and two the second. During the first penetrometer push, the vacuum pump, while drawing soil vapor into the sensor cavity, pulled water into the vacuum tube up to the surface. The source of the water was attributed to the previous days rain having saturated the soil layer. Even though the sensor continued to respond as the depth of the probe changed, it was unclear as to whether the sensor's response was due to changes in vapor concentration, water contamination, or extraneous water-related effects.

At the start of the second day, a new sensor element was placed in the sampling probe and a second sampling tube was configured to allow *in situ* air purging of the sensor cavity. This capability was added both to push clean ambient air for reestablishing baseline in the sensor cavity and to push water out of the sensor cavity. The penetrometer pushes on the second day were made in the same location as the first; however, no water was observed. As the sensor was being pushed into the ground, 5 to 10 minute sensor stabilization times were used at each measurement depth. Vapor sampling was accomplished by pulling a vacuum on the sample cavity for 1 to 2 minutes and then allowing the cavity to return to baseline atmospheric pressure via extraction of vapor from the soil. In sandy soil pulling a vacuum in the cavity was not possible. However, VOC containing vapor was extracted into the cell at approximately 100 to 200 cm<sup>3</sup>/min. In the clay strata, a vacuum of 15 to 20 in. Hg was possible.

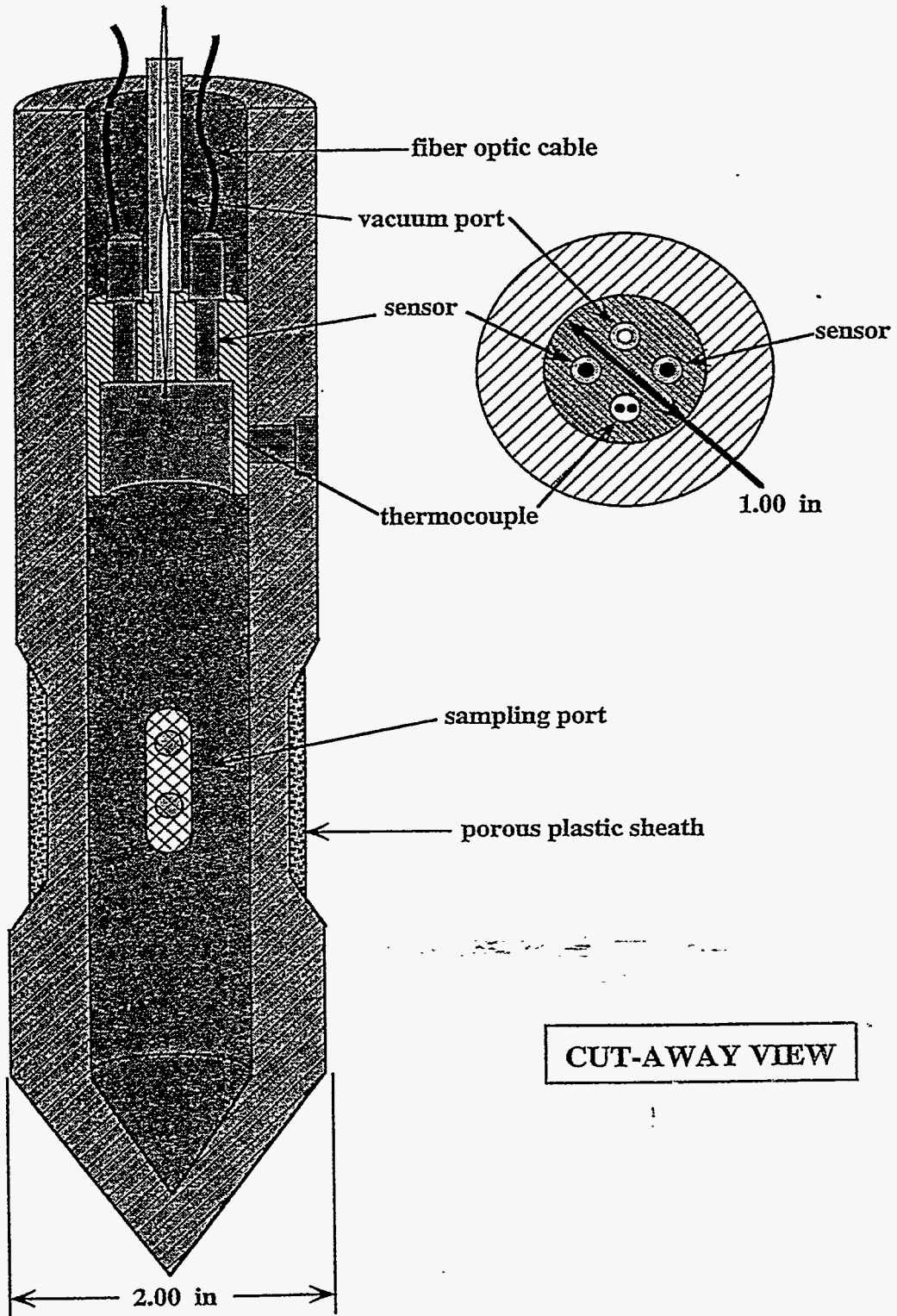


Figure 6. Schematic of demonstration cone penetrometer probe.



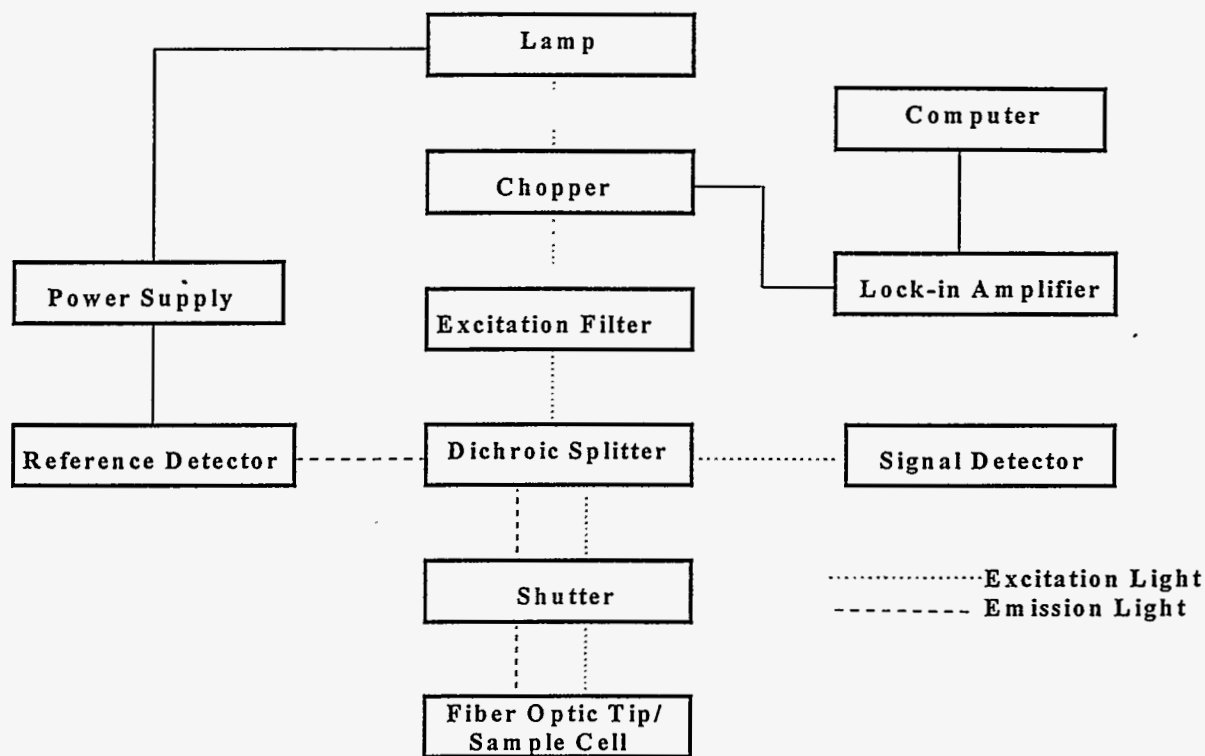


Figure 7. Schematic of optical detection system.

Under these conditions, the observed sensor response indicated VOC concentrations at 2000 to 5000 ppm. These concentrations were consistent with previously reported concentrations of 1000 to 7000 ppm in the vicinity. Several hours of *in situ* testing were performed to establish the sensor's response characteristics and stability. A combination of vadose zone vapor extraction and surface air purging was used to cycle the sensor response. When the probe was removed from the bore hole, we observed a moist sand layer compressed around the porous plastic sampling port sheath. No significant quantity of water was observed dripping from the probe, unlike the first day.

Conclusions from this initial demonstration were that the GEO-CENTERS/INEL vapochromic VOC sensor is a viable screening tool for detecting chlorinated hydrocarbons in the vapor phase. Also, the rudimentary probe configuration was a major limitation in that the sampling cavity could not be completely isolated from the sampling port and that there were few capabilities to make corrections for sampling matrix affects.

#### 4. PLANNED DEMONSTRATION OF IMPROVED FLUORESCENCE DETECTION SYSTEM

The second demonstration of this *in-situ* VOC sensor system is tentatively scheduled for the end of June 1996 at the Army Environmental Center's Aberdeen Proving Ground Test site. This demonstration will use an improved sensor configuration that addresses the issues identified during the Dover demonstration. Improvements to the VOC sensor system are as follows: 1) The sensor will have the sensor element coupled directly to the fiber optic with a polymeric material to avoid index of refraction interferences if non-gas phase

material (e.g., water) enter the detection cell. 2) Two types of substrates for the fluorescent indicator will be tested to determine if the selectivity of the sensor can be controlled by altering the permeability of the substrate. 3) The fluorescence detection optics will be configured to reduce matrix effects by recording the ratio of the fluorescence response at two wavelengths. 4) The detection optics will also be configured to measure fluorescence lifetimes, to determine the potential to simplify the source and detection optics.

The demonstration is envisioned to have the optical sensor installed within a cone penetrometer sampling probe to record a gas phase total VOC profile during a penetrometer sampling push. The concentration measurement range expected for the demonstration is 100 to 30,000 ppm of total VOCs (chlorinated hydrocarbons). The probe will be configured with one or two fiber optic sensors (containing the indicator materials to sense VOC gases), a purging tube (allowing the introduction of standard gases to the sensor or purging the detection cell with ambient air), and a polymeric screen (minimizing water and soil debris entering the detection cell). The fiber sensors and purge tube will be connected to fluorescence detectors and a vacuum pump at the surface.

## 5. ACKNOWLEDGMENTS/DISCLAIMER

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