

**Chemical Sensor and Field Screening Technology  
Development: Downhole Photoionization Detection of  
Volatile Organic Compounds**

**Topical Report  
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## EXECUTIVE SUMMARY

Western Research Institute conducted a study to define the various parameters that need to be considered in the design and use of a downhole submersible photoionization detector (PID) probe to measure volatile organic compounds (VOCs). Detector response under various conditions, including saturated humidity environments, temperature, and analyte concentration was studied. The relative responses for several VOC analytes were measured. The partitioning of VOCs between water and air was studied as a function of analyte concentration and temperature. The Henry's law constant governing this partitioning represents an ideal condition at infinite dilution for a particular temperature. The results show that this partitioning is not ideal. Conditions resulting in apparent, practical deviations from Henry's law include temperature and VOC concentration.

Studies with membranes show that membranes that allow passage of VOCs also allow some passage of water vapor. A membrane could play a useful role in protecting the sensor from direct contact with liquid water down hole. A porous poly(tetrafluoroethylene) (PTFE) membrane allows for a rapid passage of VOCs. The rate of diffusion to the sensor with or without a membrane might be a limiting factor for rapid measurements. Various means of mixing may need to be considered.



## OBJECTIVES

The objectives of this study were to define the variables that need to be considered in the design and use of a downhole submersible photoionization detector (PID) probe to measure volatile organic compounds (VOCs). These include the performance of prototype probes under a variety of conditions, the partitioning of VOCs between water and air, and various means of protecting a probe from exposure to liquid water.

## INTRODUCTION

### Volatile Organic Compounds as Key Indicators

Studies of data from 500 sites show that volatile organic compounds (VOCs) are the most significant organic contaminants in groundwater associated with disposal sites (Plumb 1992). These represented 75% of events involving organic contamination in Superfund and Resource Conservation Recovery Act (RCRA), and municipal landfill sites. Plumb (1992) found an identical mathematical relationship between VOCs and organic priority pollutants detected. He suggests that monitoring for VOCs be used as an early warning system for excursions, to indicate the need for more extensive laboratory analysis for organics, and that statistical considerations show that this will work correctly more than 90% of the time.

The extensive work leading to the conclusion that key VOC indicator monitoring could eventually replace some current indicator monitoring strategies was led by R. Plumb under a Lockheed contract to the Environmental Protection Agency. The top 18 VOCs of interest are listed in Table 1 (Plumb 1991). A similar, but not identical list was developed for sites in Germany (Kerndorff et al. 1992).

The trend towards monitoring volatile organic compounds as key indicators for excursion events provides an opportunity for the development of simple and reliable monitoring instrumentation. The devices must be able to detect VOCs either in groundwater or in the headspace above the ground water. Headspace can be either in the air above the water table in a well, or a headspace artificially created below the surface of the water by a membrane or other device. The principle of operation for a passive headspace device is Henry's law, which states that the partial pressure  $P_i$ , or concentration of a volatile component in the headspace is proportional to its concentration in the aqueous solution  $C_i$ :

$$P_i = H_i \times C_i$$

**Table 1.  $H_i$  and PID Detectability for Volatile Organic Compounds**

Compound	$H_i$ (vppm/mg/L), 25°C (77°F) <sup>a</sup>	PID Detectability	
		10.6eV	11.7eV
Dichloromethane (Methylene chloride)	29.2	N	Y
Trichloroethene	88.8	Y	Y
Tetrachloroethene	162	Y	Y
trans-1,2-Dichloroethene	57.4	Y	Y
Trichloromethane (Chloroform)	33.9	N	Y
1,1-Dichloroethane	59.2	N	Y
1,1-Dichloroethene	253	Y	Y
1,1,1-Trichloroethane	206	N	Y
Toluene	69.0	Y	Y
1,2-Dichloroethane	11.9	N	Y
Benzene	70.9	Y	Y
o-Xylene	70	Y	Y
Ethylbenzene	75	Y	Y
Vinyl chloride	11,000	Y	Y
Carbon tetrachloride	148	N	Y
Chlorobenzene	31.8	Y	Y
p-Dichlorobenzene	10.7	Y	Y
Naphthalene	3.5	Y	Y

a. Derived from: Dean 1973, Dreisbach 1961, and Weast et al. 1971

where  $H_i$  is the Henry's law constant for component  $i$ . The assumptions in using this approach for determining VOCs are that they have not exceeded their solubility in water and that they partition into the headspace according to Henry's law. The Henry's law constants for several VOCs are provided in Table 1. The units used here for  $H_i$  relate the vapor (particle) parts per million (vppm) level in the headspace to the mg/L concentration in water. Thus, the vapor concentration of toluene in equilibrium with a 1 mg/L aqueous toluene solution at 25°C (77°F) is 69 vppm. By measuring the vppm of volatile organics in the headspace above aqueous solutions of these materials, the aqueous level can be established. This assumes, however that  $H_i$  does not vary with concentration and that appropriate temperature corrections can be made. In reality, the apparent  $H_i$  does vary under certain conditions.

### Current Methods

Several approaches have been proposed for downhole monitoring of VOCs in the field. One approach uses refractive index attenuation on a coated optical fibers (Le Goullon and Goswami 1990, Oxenford et al. 1989). Another probe uses a chemical reaction in a basic medium to form a color in the presence of trichloroethylene (Milanovich et al. 1986). A radio frequency-induced helium plasma optical emission spectrometer has been designed to measure some volatile chlorinated compounds (Olsen et al. 1989). Another probe uses a heated  $\text{LaF}_2$  doped element heated to 600°C to measure volatile chlorine containing compounds (Stetter and Cao 1990). The above devices all contribute some progress towards resolving the problem of monitoring for some of the VOC indicator compounds at various levels, but all have limitations.

The purpose of the current work is to design, evaluate, and construct instrumentation based on photoionization detection for monitoring selected VOCs in groundwater at least to the low mg/L high  $\mu\text{g/L}$  level. The ionization potentials for these compounds determine whether or not they can be detected by sensors with 10.6 eV or 11.7 eV PID lamps. The compounds listed in Table 1 that can be detected in this manner are noted. The chlorinated aliphatic hydrocarbons, which do not possess a double bond, can be ionized with a higher energy 11.7 eV lamp (Driscoll and Becker 1979). Although these are available, the lithium fluoride window material required is susceptible to water vapor damage. This results in a short lamp life, which precludes its routine use. Thus, only the 10.6 eV lamp with a more stable magnesium fluoride window was chosen for the current work. Additional approaches will be needed to measure the chlorinated aliphatic hydrocarbons.

The detector system must also be able to work in an environment of varying and often high relative humidity. Response characteristics and background levels must be evaluated at different relative humidities.

## EXPERIMENTAL DETAILS

### Detector Design

Various configurations of photoionization detectors were designed and built as part of this study. The main differences were the position and geometry of the accelerator and collector and the presence or absence of a flow-through system. The humidity, inert gas/air, concentration and temperature studies were performed with a PID lamp current of 0.25 mA.

### Electronics

The electronics consisted of an electrometer, a high-voltage power supply, and control circuitry. The electrometer provided the accelerating voltage (~100 V DC) and measured the current in the collector circuit. The electrometer was a Keithley model 617.

The high-voltage power supply was a Bertan model 230-03R. This provided the voltage for starting the lamp (~1,100 V DC) and operating it (~300 V DC).

### Gas Chromatographs

The gas chromatograph (GC) used for the determination of toluene for the PID response experiments was a Hewlett-Packard 5890A equipped with an HNU PI-52, 10.6 eV photoionization detector. The column was a J&W DB-624 30 m x 0.53 mm operated isothermally at 75°C (167°F). Standardization was with toluene standards in methanol solution. The GC results were not affected by the presence or absence of water vapor in the sample.

The gas chromatograph used to determine the VOC mixtures for the membrane equilibrium studies was a Hewlett-Packard 5890A equipped with a flame ionization detector. The column was a J&W DB5 30 m x 0.53 mm operated at 40°C (5 min) ramped to 140°C at 10°/min. Standardization was with the appropriate VOC in methanol solutions.

### Chemicals

Distilled water was prepared by passing tap water through a carbon absorption bed prior to distillation in an all-glass apparatus with Teflon tubing. It was stored in glass containers prior to use. Methanol was reagent grade from commercially available sources. The VOC standards were reagent grade or better from commercially available sources.

## RESULTS AND DISCUSSION

### Initial PID Prototype Studies

Following some preliminary efforts with early prototypes, two prototype down hole PID detectors were designed for testing. These used 10.6 eV lamps with 6.9 mm  $\text{MgF}_2$  window diameters (EG&G FK-794U) and were designated PID3 and PID4. The main difference between the two was that PID4 had the collector separated from the window by a thin Teflon washer to maximize sensitivity, while PID3 had a solid Teflon insulator providing more separation between the window and the collector to minimize response to water vapor. A schematic of a typical PID is shown in Figure 1.

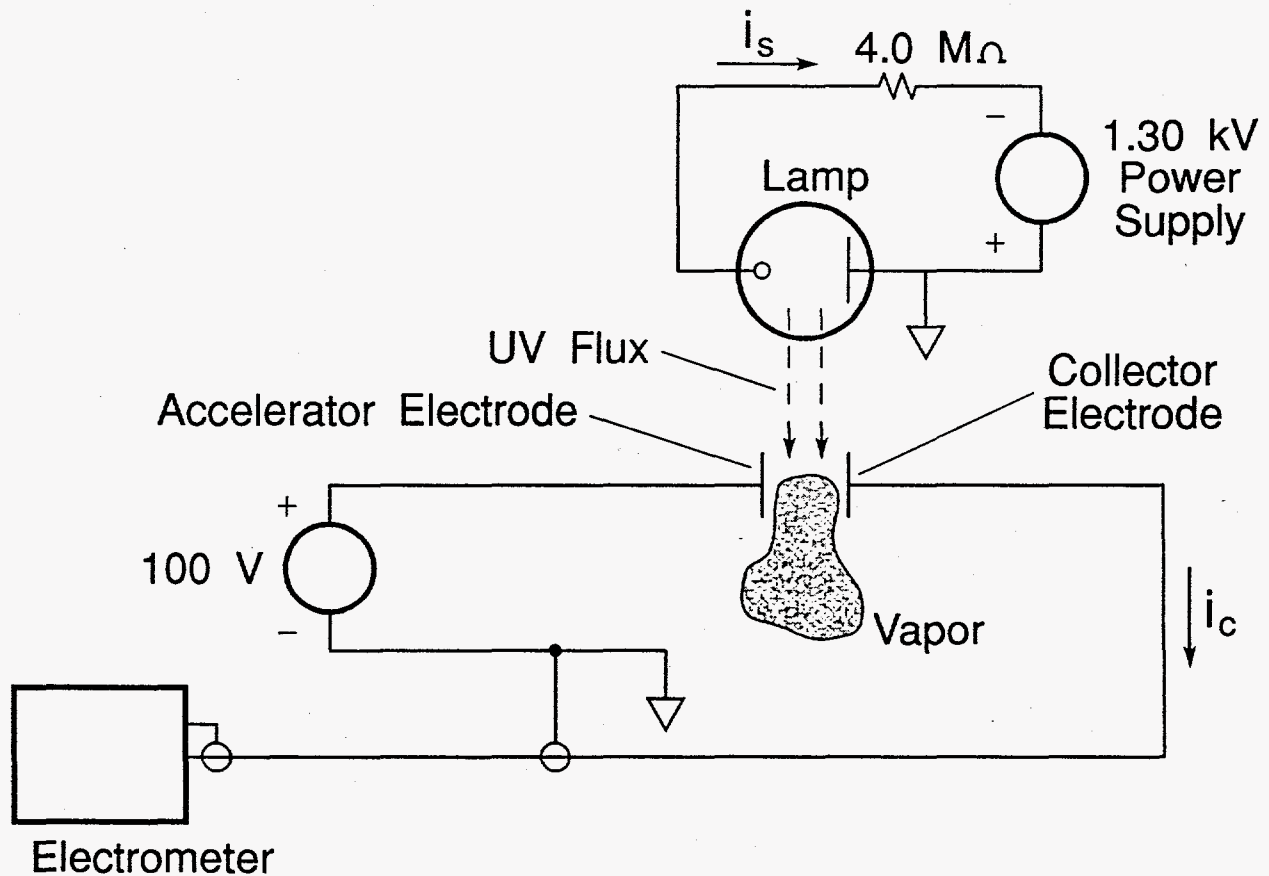


Figure 1. PID Sensor Schematic

A custom test cell combining the PID detector and septa for sample introduction and GC sampling was constructed of aluminum (Figure 2). The volume of the apparatus, including the six ports and top was 174 cm<sup>3</sup>. For the experiments relating toluene concentration to PID response, portions of toluene vapor above a pool of liquid toluene in a separate glass container were injected into the chamber through the uppermost septum port and allowed to equilibrate for 15 minutes. The required equilibration time was determined experimentally by measuring the toluene vapor concentration above a liquid pool of toluene at all six septa ports as a function of time.

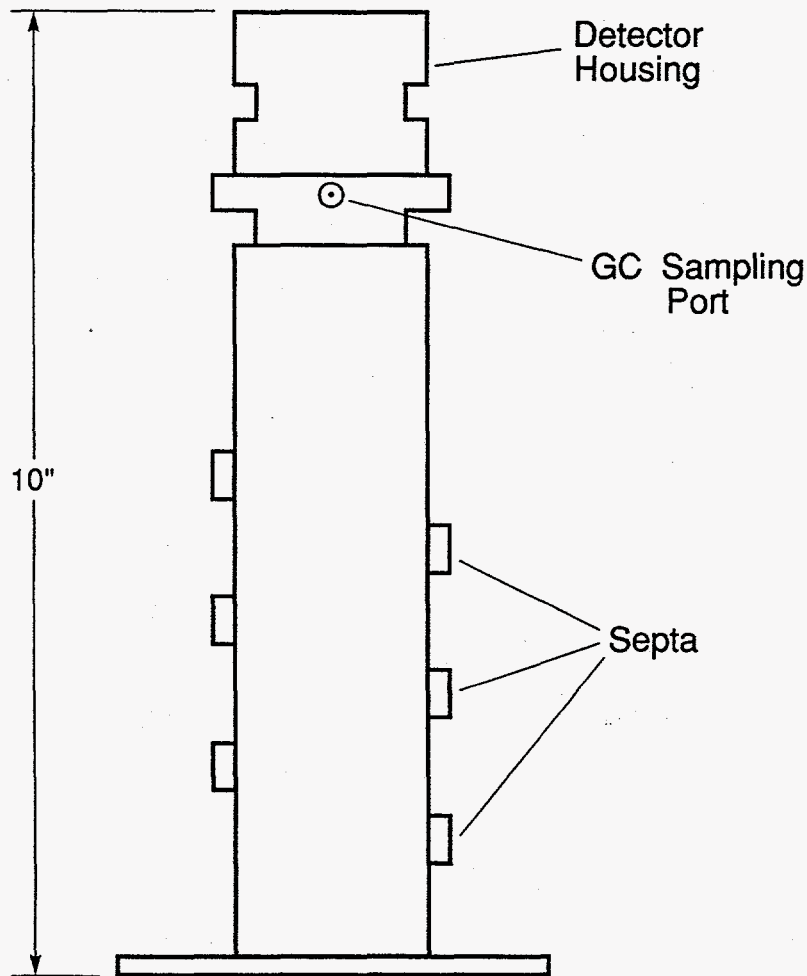


Figure 2. Sensor Test Cell Apparatus

Immediately after reading the response from the PID sensor, a vapor sample was drawn from the detector cell through a small hole sample port blocked by a Teflon plug when not in use. The sample was injected into the GC/PID instrument, and the actual concentration was measured. The experiments with toluene were conducted with and without the presence of saturated water vapor conditions. For saturated water vapor conditions, a jar containing 30 mL pre-boiled water was placed in the equilibrium chamber overnight. Toluene vapor was injected into the uppermost septum port as opposed to making solutions of toluene in water. Even below the solubility limit of toluene in water of 514 mg/L at 20°C(68°F)(Mackay and Yeun 1983), an aqueous solution could not be made directly. Each attempt resulted in some toluene floating to the surface of the water and evaporating to give artificially high readings of vapor above toluene liquid. This was probably due to a slow rate of dissolution.

A typical response profile for PID3 in dry air conditions is shown in Figure 3. The response is not quite linear. During the course of these studies, the lamps were subjected to alternate exposures to saturated water vapor conditions and dry air. The behavior of the lamps was reversible. By using dry air to purge the PID4 sensor after continuous exposure to saturated water conditions for six weeks, the dry air response conditions were restored. Some typical results extracted from the many measurements made with PID3 and PID4 are provided in Table 2.

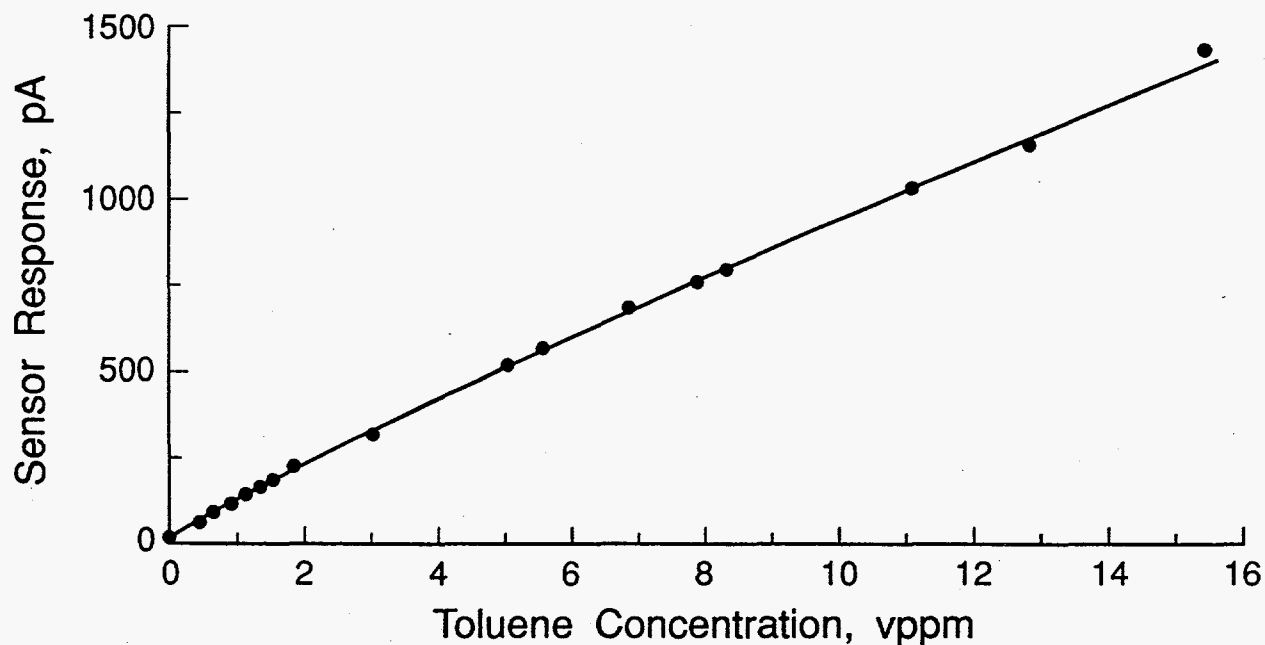


Figure 3. Typical PID Sensor Response Profile

**Table 2. Typical Detector Response Characteristics at Room Temperature**

Detector	Background, Current, pA	Sensitivity, pA/vppm Toluene	pA Output at 1 vppm Toluene
<u>PID3</u>			
Dry	24	100	124
Wet	39	32	71
<u>PID4</u>			
Dry	137	360	497
Wet	2,990	160	3,150

The background and sensitivities vary slightly over a series of measurements. The sensitivities were measured in pA at toluene concentration levels of about 2-30 vppm and were calculated to response per vppm for comparison, assuming a linear response in the region of interest. For both PID3 and PID4, saturated water vapor conditions decrease the sensitivity by at least a factor of two. For the same set of conditions (wet, dry), the sensitivity of PID4 is at least three times higher than for PID3. Water vapor has a dramatic effect on the background current for PID4, however, which would make it difficult to interpret a signal from this detector. The effect on PID3 is less dramatic. It appears possible that a significant signal could be observed for a toluene level above 1 vppm. The PID3 design was less affected by water vapor, and thus could be used as a sensor in a probe design. Thus, although having the collector near the window results in greater sensitivity in dry air, any advantage is lost in high humidity environments. These results indicate the desirability of excluding water vapor from the measurement system or using a probe design that is minimally affected by water vapor.

The response characteristics of PID3 and PID4 in dry air were compared to the responses in inert gases, which do not contain oxygen which absorbs the ionizing light. Measurements were made at toluene levels ranging from 1 to 3 vppm. The results are listed in Table 3. For PID3, the background (photoelectric) currents are similar in argon and nitrogen, but lower for air. For PID4, the background currents are similar in air and nitrogen. For PID3, the sensitivities to toluene are similar for both inert gases and lower in air. For PID4, the sensitivities in nitrogen are greater than the sensitivities in air. These observations can be related to the presence of oxygen in air, which absorbs a significant amount of the ionizing radiation in PID3, where the collector was mounted farther away from the window than in PID4, where the collector was mounted near the window.



**Table 3. PID3 Response With Various Gaseous Environments at Room Temperature**

Detector	Gas	Background, pA	Sensitivity to Toluene, pA/vppm
PID3	Air	32	125, 108
	N <sub>2</sub>	67	170, 185
	Ar	78	181, 204
PID4	Air	166	356, 384
	N <sub>2</sub>	153	460, 465

To further characterize the response of PID3 over time, the detector was kept in a saturated humidity environment for about two months. The background signal and response to toluene vapor under both dry and high-humidity conditions were measured before and after this period (Table 4). The results show that although there was some change over time in the high-humidity environment, the dry response conditions were restored upon purging with dry air.

**Table 4. PID3 Detector Response Characteristics Over Time at Room Temperature**

Condition	Elapsed Time	Background Current, pA	Average Sensitivity pA/vppm Toluene
Dry Air	Start	29	107
100% Humidity	2.5 Hrs.	59	33.0
	16 Hrs.	46	36.9
	56 Days	35	52.7
Dry Air	56 Days	36	110

## Sparger Studies

To study the performance of the PID sensors under saturated humidity conditions with vapor in equilibrium with water, a sparger apparatus was constructed. A schematic diagram of the device is shown in Figure 4. Except for the sensor and housing, all wetted parts are Teflon, glass, or stainless steel. The pump was an ASF pump with Teflon diaphragm. The volume of water used was 4.000 L, which constituted about 91% of the total system volume of 4.402 L. To test the device, PID3 was used as the sensor, and various volumes of toluene vapor were injected into the water with the pump on at an air flow rate of ~4L/min (Table 5). Both PID3 sensor and GC readings were taken at 3 minutes after injection. Preliminary studies showed that equilibration time is 1 minute, and there was no noticeable loss of toluene vapor in the system within a 5-minute test interval. The results show a lower saturated water background for PID3 than in Table 2, with a signal of 3x this background corresponding to 0.57 vppm toluene. Possibly this is due to the movement of air across the sensor. Experiments also showed that when the sparger pump was shut off, the signal from PID3 dropped dramatically within a few seconds. We believe this is probably caused by the depletion of sample in the light path due to ionization/destruction of the toluene vapor.

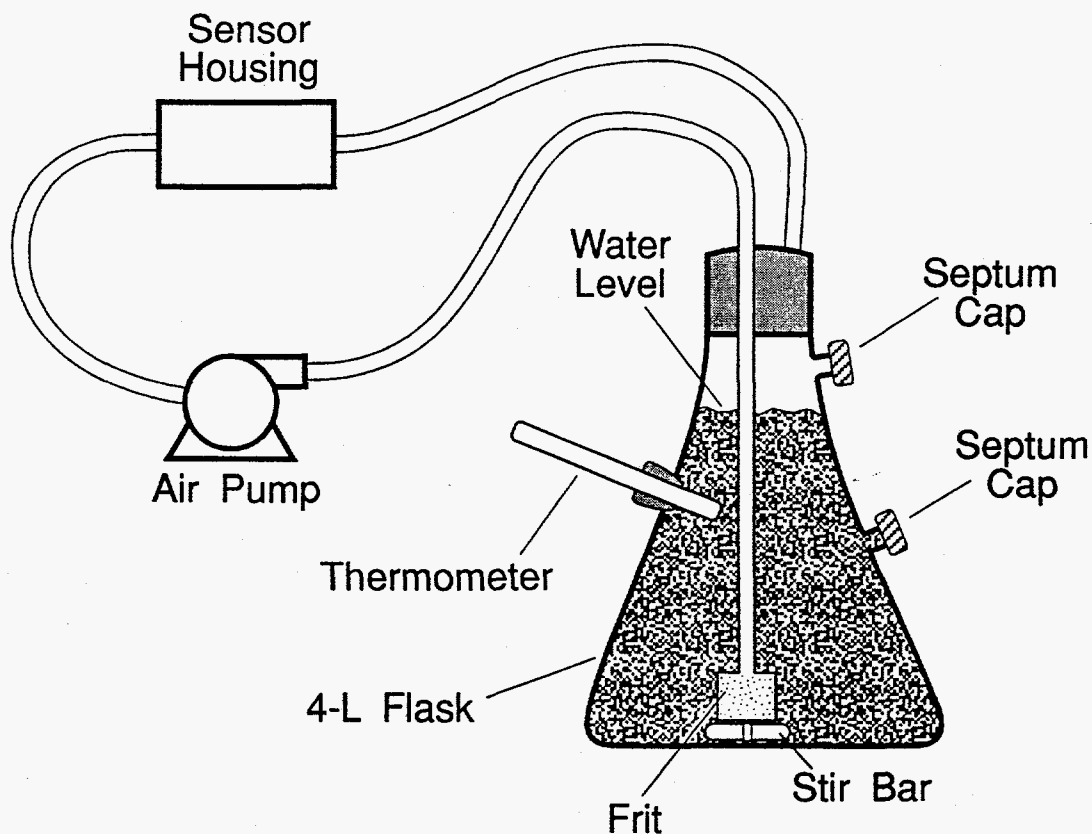


Figure 4. Sparger Apparatus for Sensor Response Evaluation

**Table 5. PID3 Response in Sparger Apparatus at Room Temperature**

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Toluene Concentration, vppm <sup>a</sup>	PID3 Response, pA
0.00 (blank)	14
0.45	30
0.57	42
1.0	60
1.4	78
1.5	86
2.9	145
5.5	237
7.1	307

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a. Measured by Gas Chromatography

### Henry's Law Constants

The sparger apparatus was used to evaluate Henry's law constants for VOCs of interest under a variety of conditions. Henry's law constants are defined as infinite dilution and can vary with concentration (Nielsen et al. 1994). Preliminary studies were conducted with toluene to establish optimal experimental conditions. To calculate an  $H_i$  value, a portion of toluene was injected into the sparger with the stirrer and recirculating pump on. The concentration of toluene in vppm was determined by GC in the headspace and was divided into the concentration of the toluene in the water in mg/L based on the amount of toluene added to the water. The initial concentration in the water was corrected for the amount of toluene found in the headspace. For 4.000 L water volume and 402 mL headspace volume, the corrections were made for only about a 1-2% decrease in concentration resulting from the volatilization of a small amount of toluene into the headspace. This is much smaller than the total estimated combined analytical error of 10% from the standardization and determination of toluene vapor concentrations by GC. In the few cases where experiments were set up with the headspace comprising more than 10% of total system volume, the correction for depletion of the VOCs in water was more significant.

Preliminary experiments showed that results from injections of toluene did not differ significantly from injections of liquid toluene, toluene vapor, 10% (vol./vol.) weighed toluene in methanol solutions. Dewulf et al (1995) found that the use of VOC standards in methanol does not

affect the results of  $H_i$  measurements. The injection of portions of a 10% toluene solution in methanol is easier to control accurately than injections of headspace vapor or pure liquid toluene. Some work was performed to confirm that there was no significant difference in results from the injection of pure toluene or the more easily handled 10% toluene in methanol solution. The experiments were run at room temperature, and the actual temperature for each set was recorded. The results are provided in Table 6.

The data show that there is no significant difference in results for the liquid toluene or the 10% toluene in methanol solutions run at temperatures of 20-21°C (68-70°F). There is a difference, however for the experiment performed at 24°C (75°F). The average  $H_i$  values compare favorably with the value of 45.4 vppm/mg/L at 18.2°C (65°F) and values ranging from 59.5 to 73.6, with an average of 68.3 vppm/mg/L at 25°C (77°F) reported by Dewulf et al. (1995). The volumes of the methanol aliquots added are known to three significant figures, while the small microliter volumes of liquid toluene are difficult to measure accurately. For the subsequent experiments involving the measurement of VOC air to water partition ratios, 10% solutions of the VOCs in methanol were used.

Experiments with both toluene and trichloroethylene (TCE) were performed to define the variables involved in practical deviations from the ideal behavior described by Henry's law. The measured vapor-to-liquid concentration ratios,  $H_i$ , for toluene and trichloroethylene are shown as a function of concentration at various temperatures in Figures 5 and 6, respectively. As the concentrations in water increase,  $H_i$  decreases. One possible reason for this apparent non-ideal behavior is that as the concentration VOCs dissolved in water increases, the water becomes no longer pure water. The mixture can effectively retain more VOCs in solution than would be predicted by the ideal  $H_i$  value, which is defined at infinite dilution. The effect of a relatively small amount of material dissolved in a pure solvent on solvent strength and other properties is well known (Snyder 1968). The variations become more dramatic at the higher temperatures for both VOC compounds, with smaller changes in  $H_i$  occurring at the lower temperatures. At 33°C (91°F), as infinite dilution is approached for toluene, the asymptotic ratio of vppm/mg/L indicates that essentially all the toluene will enter the vapor phase (Figure 5). For purposes of downhole monitoring of headspace in water wells, however, the temperature of most interest is near 11°C (52°F), which is typical for shallow groundwater in the U.S. (van der Leeden et al. 1990). In this temperature region, deviations of  $H_i$  with concentration are apparent but not as severe as at higher temperatures.

To ensure that the concentration dependence of  $H_i$  was not specific to the sparger apparatus, similar experiments were performed in a 2000 cm<sup>3</sup> round glass flask containing 1800 cm<sup>3</sup> of water. Aliquots of toluene were added from 10% toluene in methanol solution through a Mininert valve. The flask was shaken by hand for 3 minutes in a room thermostatted to 10-12°C (50-54°F), and a sample of the air was then analyzed by GC. The results are shown in Figure 7. The data from both the sparger and the round flask are virtually identical.

**Table 6. Comparison of Sparger Results from the Injection of Liquid Toluene or 10% Toluene in Methanol (vol./vol.)**

Injection Conditions	$\mu\text{L}$ Injected	Aqueous mg/L	Headspace vppm	Hi, vppm/mg/L
Liquid Toluene, 21°C(70°F)	1.0	0.21	12.3	59
	2.0	0.43	26.8	62
	5.3	1.1	61.1	56
	9.0	1.9	118.0	<u>62</u>
Liquid Toluene, 21°C(70°F)	1.0	0.21	12.5	60
	2.0	0.43	21.4	50
	5.0	1.1	66.7	61
	9.0	1.9	118.0	<u>62</u>
10% Toluene in Methanol, 20°C(68°F)	11.0	0.235	12.6	53.6
	23.0	0.491	25.2	51.3
	53.0	1.13	65.4	57.9
	90.0	1.92	120.0	<u>62.5</u>
10% Toluene in Methanol, 24°C(75°F)	12.0	0.255	19.4	76.1
	25.5	0.542	35.6	65.7
	45.0	0.955	70.4	73.7
	95.0	2.02	144.0	71.3
	250	5.32	335.0	<u>63.0</u>

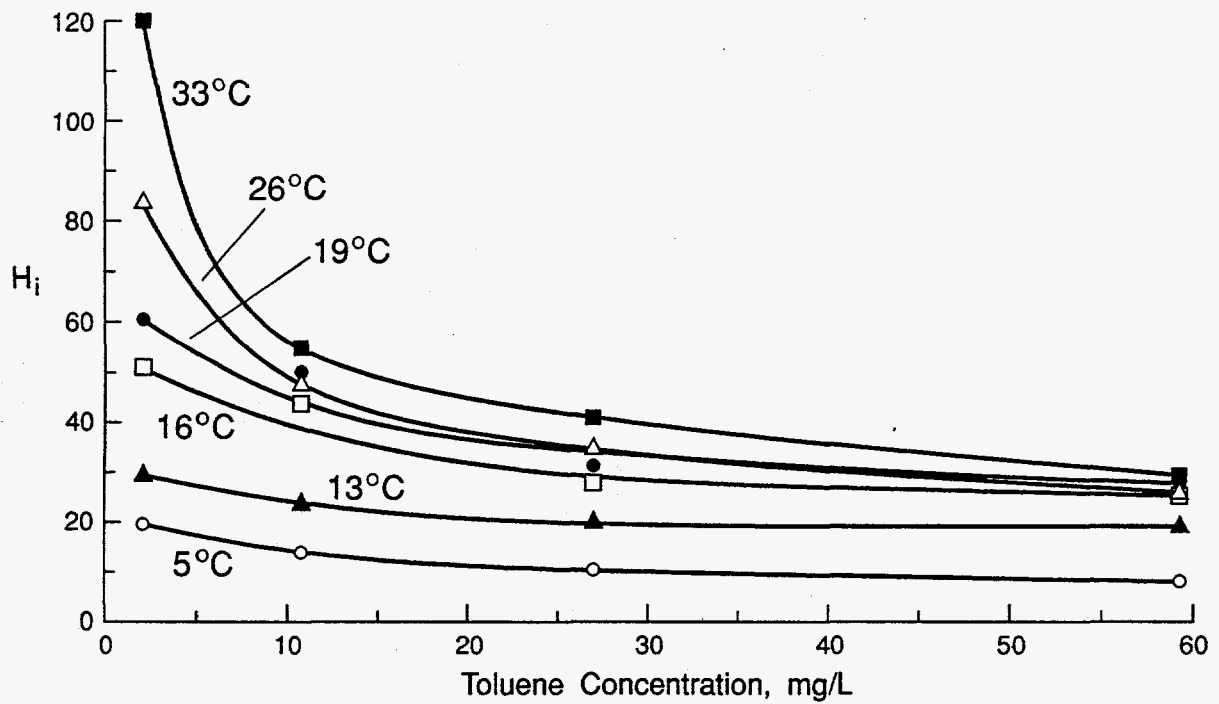


Figure 5.  $H_i$  Values for Toluene at Various Concentrations and Temperatures

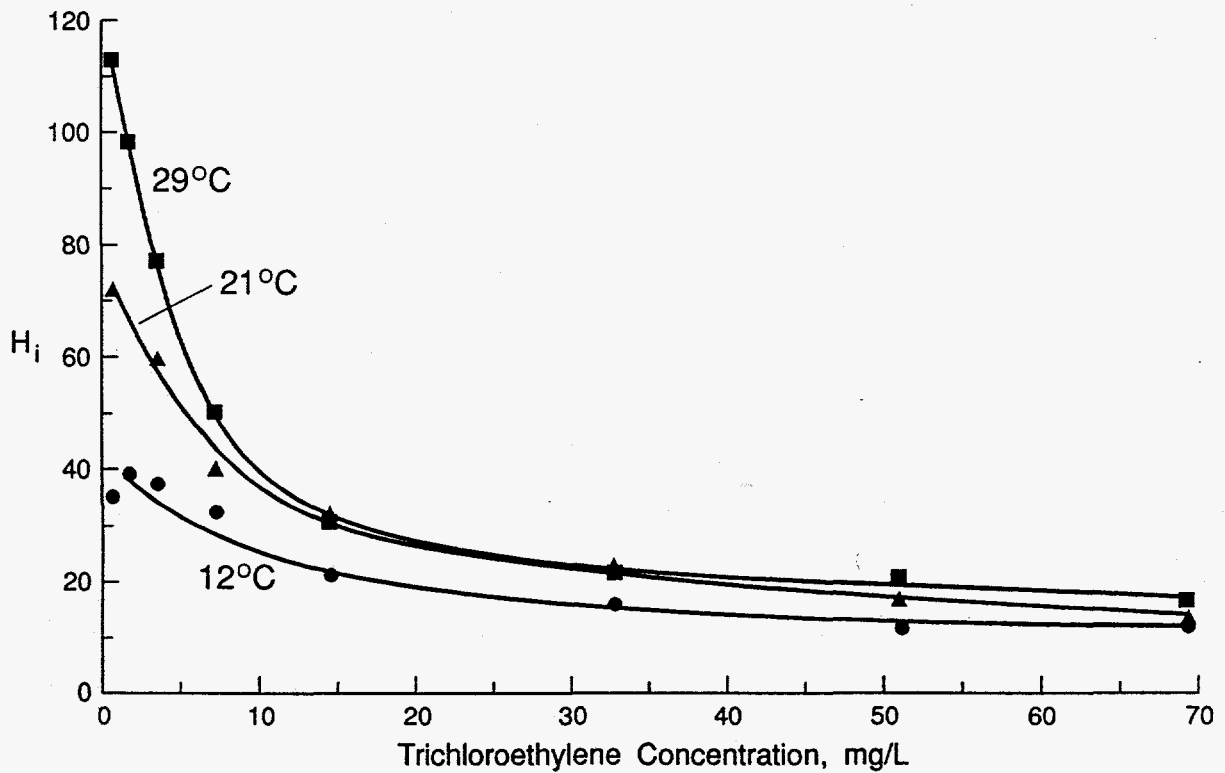
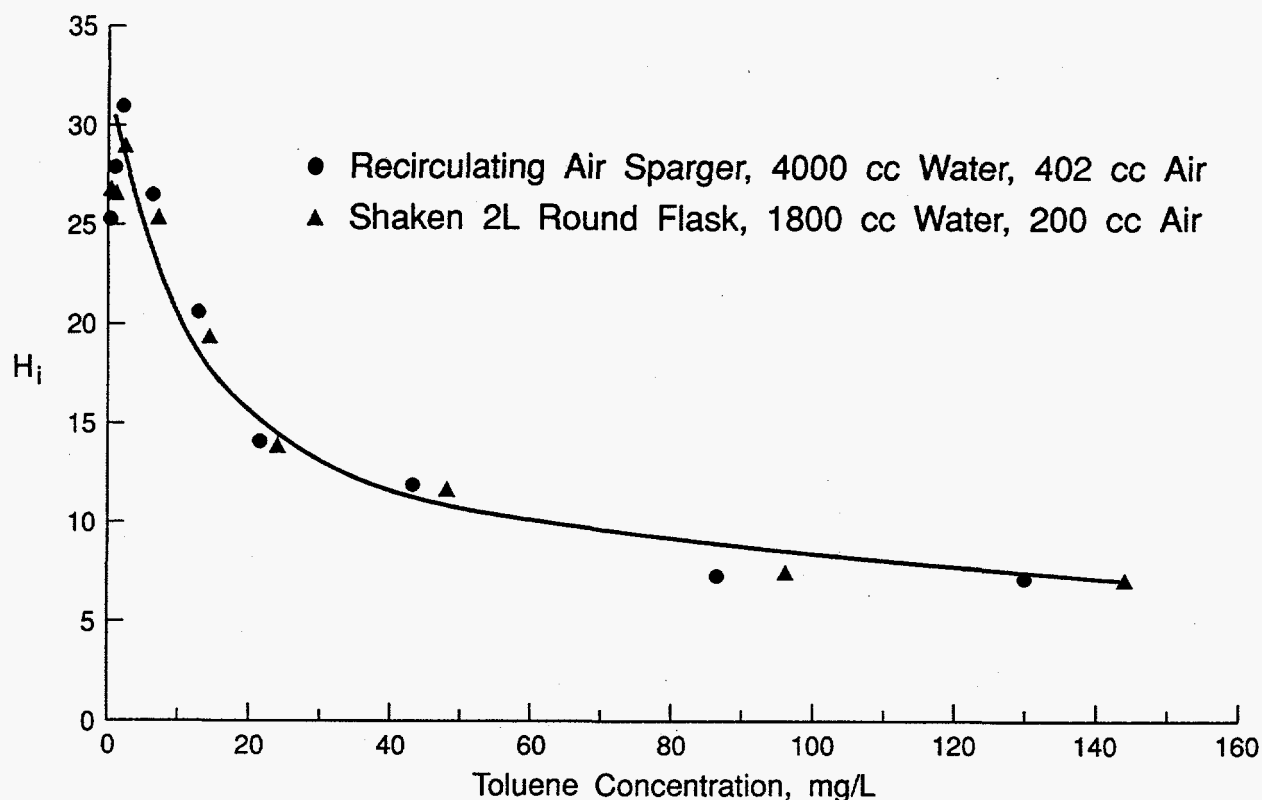


Figure 6.  $H_i$  Values for TCE at Various Concentrations and Temperatures

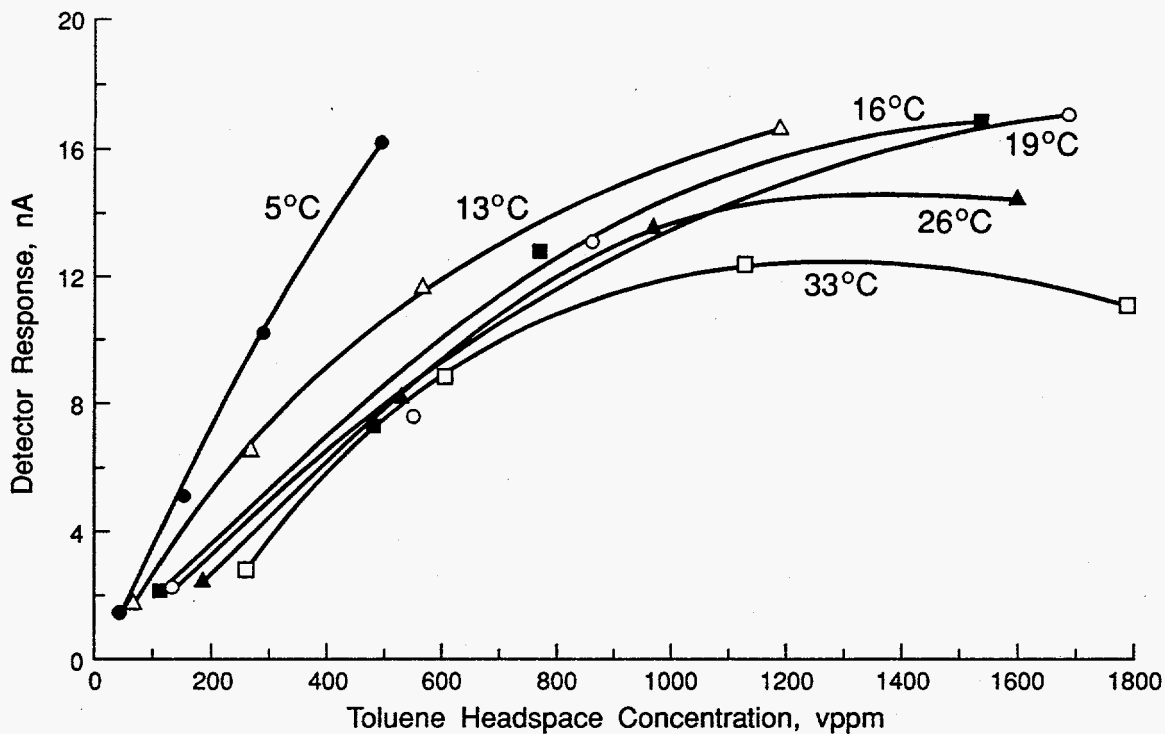


**Figure 7. Comparison of Results with Air Sparger and Shaken Flask**

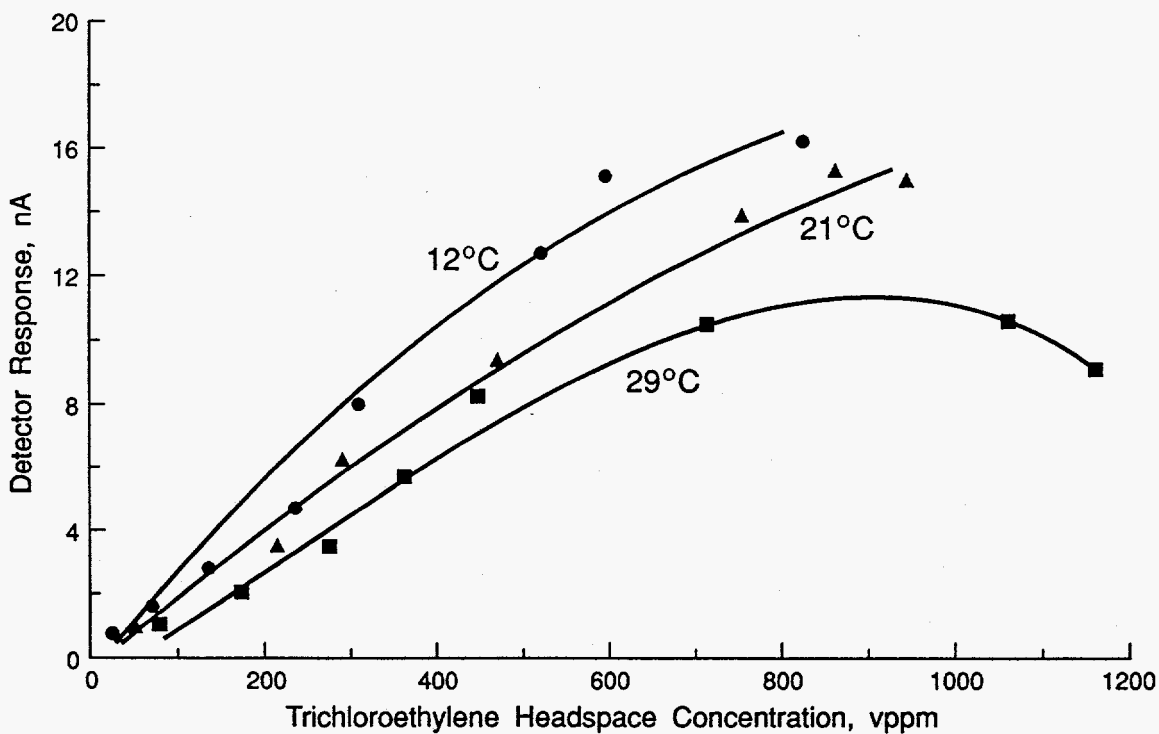
Another consideration is the response of the PID detector as a function of vapor concentration and temperature. The response profiles for PID3 in the sparger apparatus for toluene and TCE are shown in Figures 8 and 9, respectively. At the primary temperature of interest, 10-12°C (50-54°F), the detector response shows significant curvature as it increases to about 16 nA output, which corresponds to a toluene headspace concentration of about 1000 vppm or a TCE concentration of about 800 vppm. At temperatures of 29-33°C (84-91°F), the response increases initially, then decreases with increasing concentration. At 5°C, the response for toluene at 500 vppm is 16 nA and shows little curvature. The decreased response of the PID with increasing temperature is possibly due to the saturated humidity conditions inherent in the sparger apparatus. The absolute humidity, or number of water molecules in the air absorbing the excitation light, increases with temperature.

### **Measuring VOCs in Water**

The responses of detector PID3 in nA as a function of aqueous concentrations of toluene and TCE are shown in Figures 10 and 11, respectively. These response profiles are a combination of all the effects discussed above and reflect the practical interpretation of a PID headspace detector signal.



**Figure 8. Sensor PID3 Response to Toluene Vapor in a Saturated Humidity Environment at Various Temperatures**



**Figure 9. Sensor PID3 Response to TCE Vapor in a Saturated Humidity Environment at Various Temperatures**



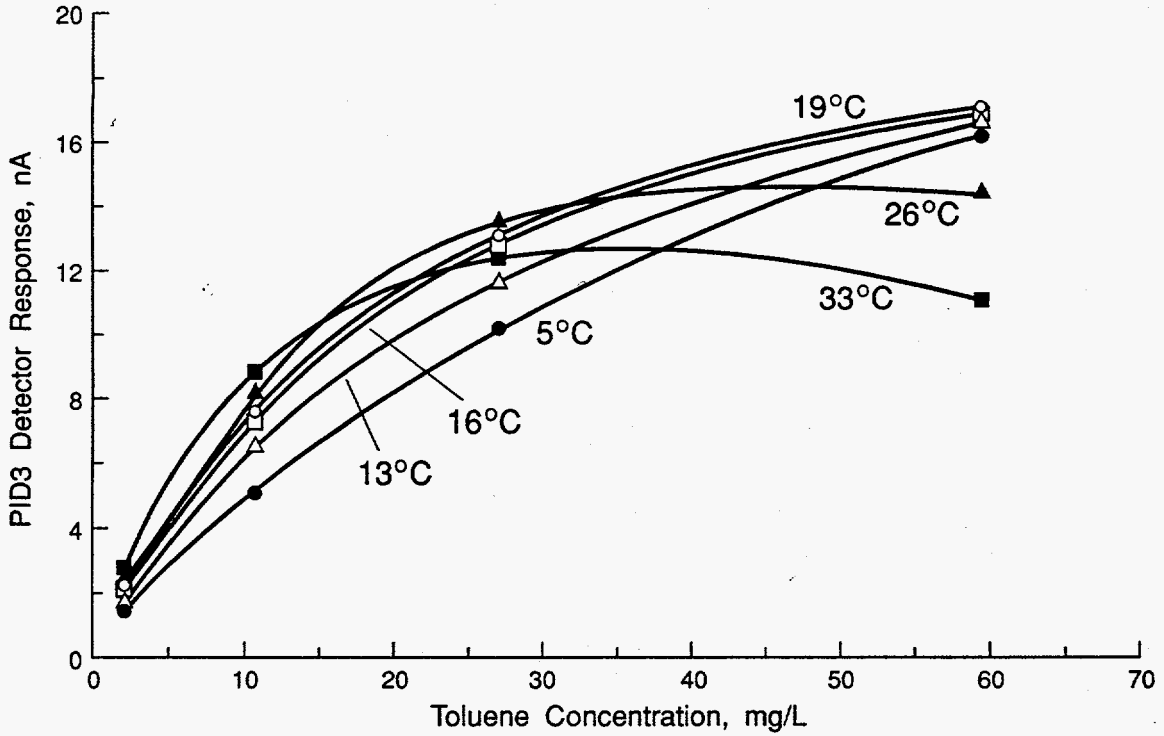


Figure 10. Sensor PID3 Response to Toluene in Headspace Above Water at Various Temperatures

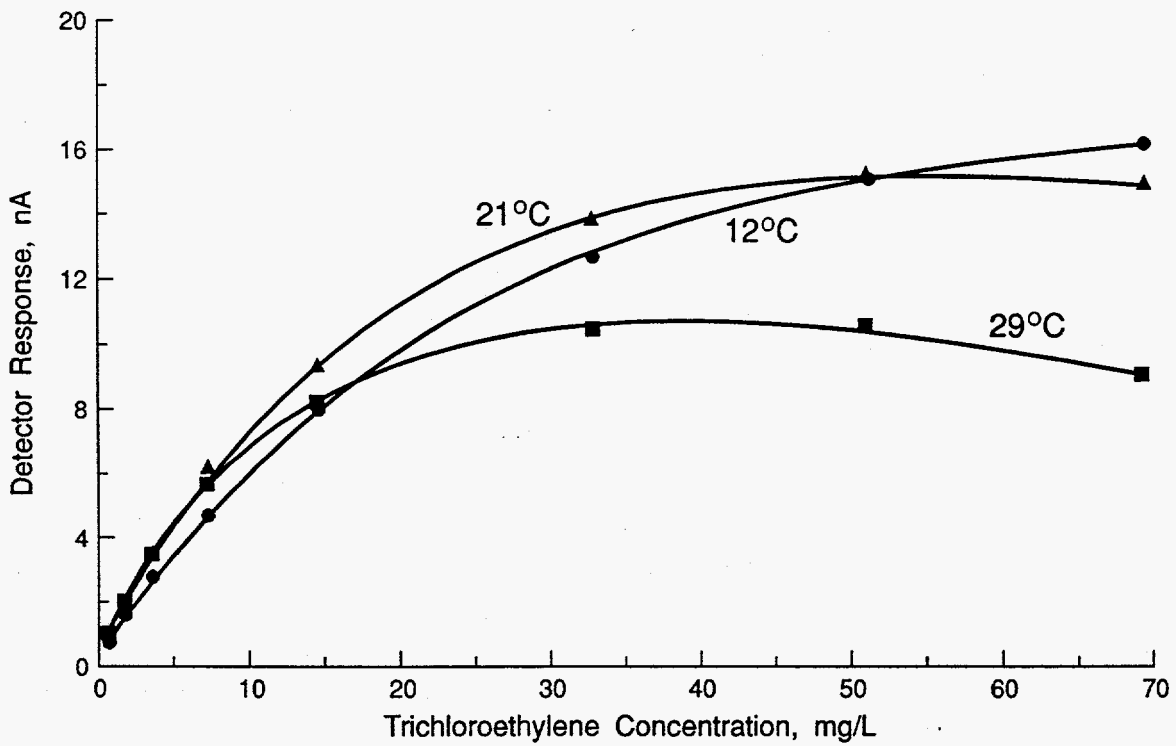


Figure 11. Sensor PID3 Response to TCE in Headspace Above Water at Various Temperatures

relative to the concentration in the well water. All of the response profiles show some non-linearity. The profiles for toluene are similar for temperatures ranging from 5 to 19°C (41 to 42°F) and show a saturation effect with concentration at 26°C (79°F) and 33°C (91°F). A similar trend is observed for TCE (Figure 11). Lists of simple relative responses for VOCs in relatively dry air have been published (Langhorst 1981 and Driscoll and Becker 1979). These cannot be used directly for relating the aqueous concentration from a probe in headspace. Interpreting the signal must take into account the identity of the component and the particular calibration/response curve, which is a function of the water temperature.

The response of detector PID3 at 12°C (54°F) in the sparger with toluene and TCE near the detection limit is provided in Table 7. The blank response was 13 pA. The data show that the detection limit is near 1 vppm for toluene and TCE, if 3x the blank signal is used as the criterion. This is an estimate only, since other criteria could be used. The data also show that the  $H_i$  values do not vary with concentration at these low water concentration levels. The average  $H_i$  for toluene is 36.0 vppm/mg/L for toluene and 41.3 vppm/mg/L for TCE (Table 7). Dewulf et al. (1995) reported values (converted to vppm/mg/L) of 26.8 at 10°C (50°F) and 45.4 at 18°C (64°F) for toluene, and 24.8 at 10°C (50°F) and 46.7 at 18°C (64°F) for TCE.

**Table 7. PID3 Characteristics at 12°C (54°F) Near the Detection Limit**

VOC Compound	Aqueous mg/L	Headspace vppm	$H_i$ , vppm/mg/L	PID3 Response pA
None (Blank)	-	-	-	13
Toluene	0.0407	1.46	35.9	70
	0.105	3.77	35.9	158
	0.210	7.58	36.1	265
	0.424	15.3	<u>36.1</u>	485
			Average:	36.0
TCE	0.0396	1.77	44.7	60
	0.0939	3.58	38.1	122
	0.187	8.00	42.8	230
	0.375	16.4	<u>43.7</u>	410
			Average:	42.1

## Membrane Studies

The possible use of membranes to prevent liquid water from reaching a sensor and to minimize the amount of water vapor in a sensor chamber was explored. Various uses of membranes for VOC measurements in water have been described (Stetter and Cao 1990, Strike et al. 1993, Anheier et al. 1993).

To study membrane behavior, some systematic membrane screening experiments were designed. A glass equilibrium chamber was built (Figure 12). A Teflon-lined septum was installed at both ends of the chamber, which was divided into two equal volume sections of 130 cm<sup>3</sup> by the membrane being tested. The membrane diameter exposed to the vapors was 29 mm. Various membrane materials were evaluated by injecting 5.0 mL of saturated organic vapors from above a liquid mixture of volatile organic compounds into one side of the membrane (side A) and measuring the vapor concentrations by GC/FID on both sides (sides A and B) of the membrane after set time intervals of 1 hour and 18 hours at room temperature. For each time interval used, a separate experiment was run.

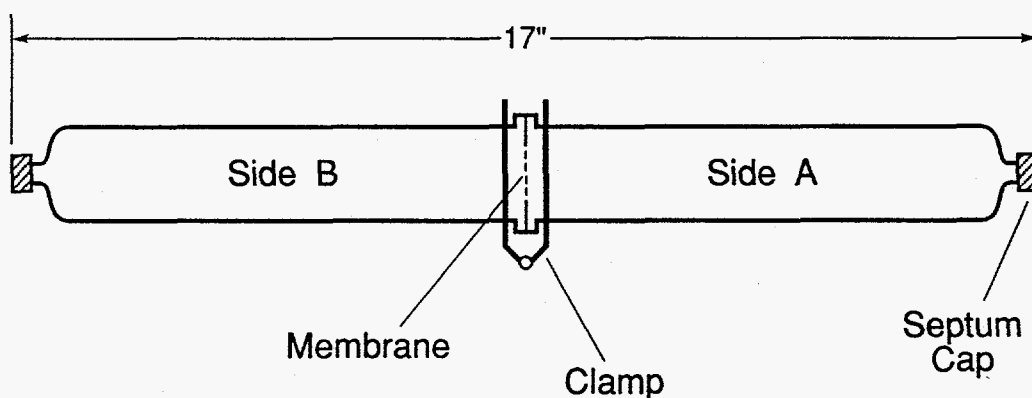


Figure 12. Equilibrium Chamber for Membrane Evaluation

Three different liquid mixtures of VOC liquids were used to provide vapors. These were chosen because the mixture components could be separated by GC, and each mixture contained some aromatic and halogenated standards, which would allow for qualitative repeatability checks when a membrane was studied with each mixture. The compositions of the mixtures are shown in Table 8, along with the results of a typical set of membrane evaluation experiments with 0.025 mm thickness polyethylene (PE). The percent area denotes the amount of area in a GC chromatogram for a compound on one side of the membrane divided by the total of the areas for that compound measured on both sides of the membrane. The membranes that were tested and their ability to pass organic vapors completely (~50% on each side of chamber) over a 1-hour and 18-hour period are shown in Table 9.

**Table 8. Permeation Results for a 0.025-mm Polyethylene Membrane**

Vapor Mixture	<u>After 1 Hour</u>		<u>After 18 Hours</u>	
	%Area Side A	%Area Side B	%Area Side A	%Area Side B
Mix 1. Methylene Chloride	91.4	8.6	—	—
Chloroform	92.5	7.5	—	—
1,2-Dichloroethane	86.3	13.7	—	—
Toluene	75.5	24.5	—	—
Mix 2. Trans-1,2-Dichloroethylene	86.5	13.5	50.6	49.4
Carbon tetrachloride	96.4	3.6	53.9	46.1
Tetrachloroethylene	75.6	24.4	49.4	50.6
Ethylbenzene	73.5	26.5	51.4	48.6
o-Xylene	72.6	27.4	48.4	51.6
Mix 3. 1,1-Dichloroethylene	91.2	8.8	—	—
1,1,1-Trichloroethane	95.0	5.0	—	—
Benzene	80.1	19.9	—	—
Trichloroethylene	72.8	27.2	—	—
Chlorobenzene	60.2	39.8	—	—

**Table 9. Membranes Studied and Their Ability to Pass Organic Vapors**

Membrane Material Description	1-Hour	18-Hour
None (control)	complete	—
Aluminum foil (control)	none	none
<u>Membranes Without Designated Pores</u>		
Polyethylene, 0.015 mm	partial	complete
Polyethylene, 0.025 mm	partial	complete
Polyethylene, 0.061 mm	partial	complete
Polypropylene, 0.102 mm	none	trace
Poly(vinylidene chloride), 0.053 mm	none	none
Poly(siloxane), 0.127 mm	~complete	—
Poly(siloxane), 0.254 mm	~complete	—
Report cover film, 0.114 mm	none	none
Transparency film, 0.107 mm	none	none
<u>Membranes With Designated Pores</u>		
Poly(vinylidene fluoride), 0.1 $\mu$ pore	complete	—
Poly(tetrafluoroethylene), 0.02 $\mu$ pore	complete	—
Poly(tetrafluoroethylene), 0.2 $\mu$ pore	complete	—
Acrylic copolymer, 50,000 Dalton pore	partial	~complete
Regenerated cellulose, 1,000 Dalton pore	trace	partial
Mixed cellulose esters, 0.025 $\mu$ pore	complete	—

For membranes exposed to saturated water vapor, the results show essentially complete water vapor passage through the membranes with pores, with less than complete passage after 18 hours for the membranes without pores (Table 10). The results show that the amount of water vapor passed by the nonporous membranes PE and poly(siloxane) in a given period is a function of the thickness of the particular membrane. For such membranes, permeation is directly proportional to the product of the area of a membrane, the pressure differential and a permeability constant and is inversely proportional to the membrane thickness (Hoch and Kok 1963). Permeation also is a function of temperature (Greenwalt et al. 1983). For the membranes exposed to water vapor, the most complete permeation to the VOCs with the smallest water vapor permeation was the 0.254 mm poly(siloxane), in one hour, followed by the 0.061-mm-thick PE, in 18 hours. The permeation of water vapor through the porous membranes that passed the VOC vapors completely in one hour was 78.7-87.3% of complete permeation in the same period. The permeation of water vapor through these porous membranes and the non-porous membranes poly(siloxane) and PE to equal levels on both sides takes longer than the permeation of the VOC vapors at the levels studied. The rates vary, however, with the passage of both VOCs and water vapor through the porous membranes being significantly faster than for the nonporous membranes.

**Table 10. Membranes Studied and Their Ability to Pass Water Vapor from Exposure to Saturated Vapor or Liquid**

<u>Membrane Material Description</u>	<u>Percent Relative Humidity</u>			
	<u>Water Vapor</u>		<u>Liquid Water</u>	
	1 Hour	18 Hours	1 Hour	18 Hours
<u>Membranes Without Designated Pores</u>				
Polyethylene, 0.015 mm	16.5	80.0	89.2	107
Polyethylene, 0.025 mm	11.4	57.0	7.9	50.5
Polyethylene, 0.061 mm	7.6	47.9	8.2	39.5
Poly(siloxane), 0.127 mm	71.4	99.2	70.9	106
Poly(siloxane), 0.254 mm	40.9	98.0	59.7	103
<u>Membranes With Designated Pores</u>				
Poly(vinylidene fluoride), 0.1 $\mu$ pore	83.5	103.9	92.0	110
Poly(tetrafluoroethylene), 0.02 $\mu$ pore	87.3	104.2	89.3	109
Poly(tetrafluoroethylene), 0.2 $\mu$ pore	78.7	97.1	93.4	107
Acrylic copolymer, 50,000 Dalton pore	73.4	99.2	91.3	108
Mixed cellulose esters, 0.025 $\mu$ pore	83.3	100.9	92.8	109

To further study the behavior of the nonporous membranes PE and poly(siloxane) and a porous poly(tetrafluoroethylene) (PTFE) membrane, one membrane of each type was studied. The membranes chosen were the 0.254-mm poly(siloxane), 0.025-mm PE, and 0.02 $\mu$  pore size PTFE. The thicker PE (0.025 mm) membrane was used, since it was stronger than the 0.015-mm-thick PE. The permeation of VOCs was studied from both aqueous solution and the headspace above an aqueous solution using the equilibrium chamber configurations shown in Figure 13.

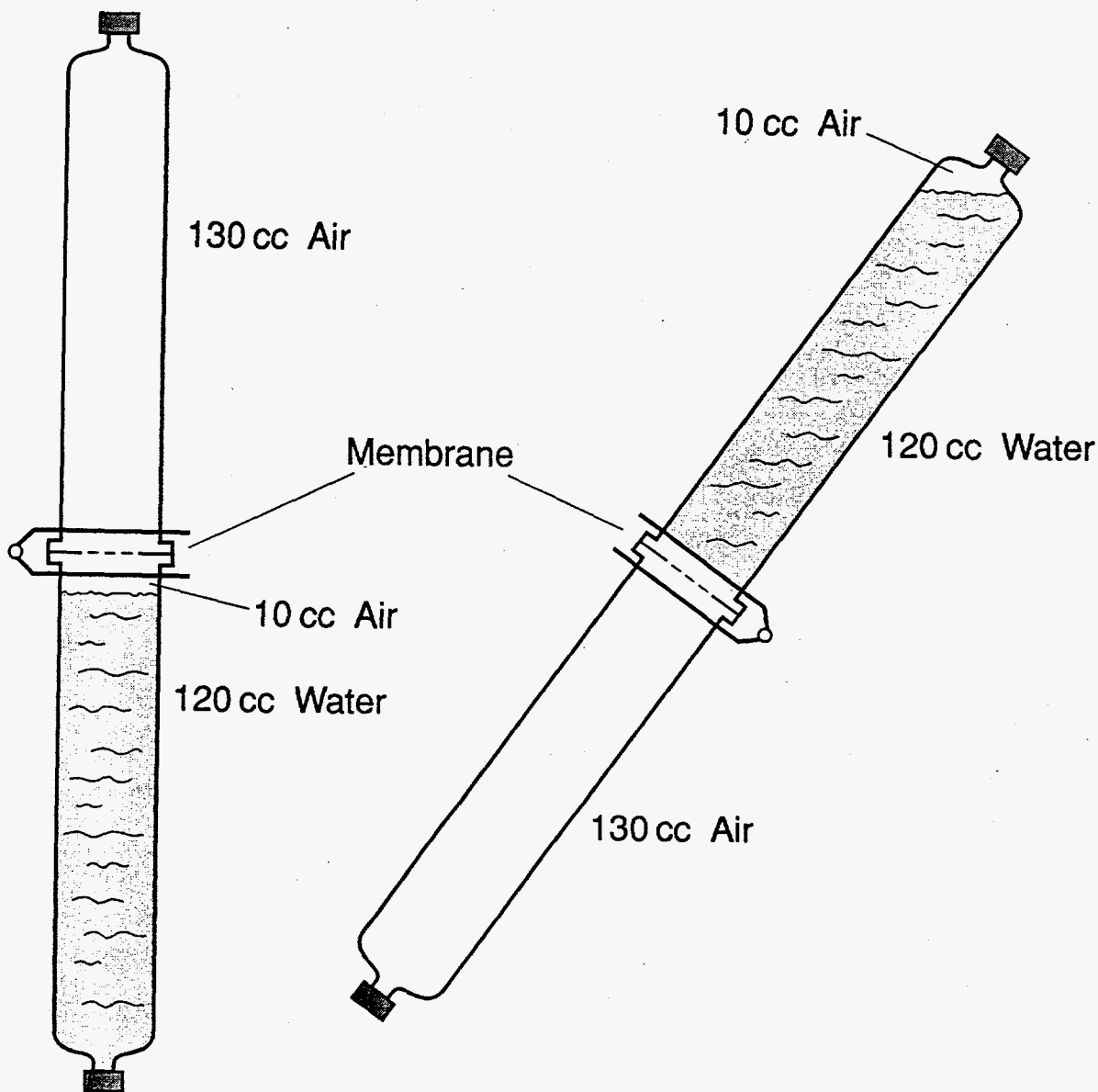


Figure 13. Equilibrium Chamber Configurations for Aqueous Solution Studies

All results were compared to the VOC vapor concentrations without a membrane in the headspace above the upright configuration of the chamber shown on the left in Figure 13. Initial studies showed that the results varied with fluctuating room temperature. Therefore, the experiments were performed in a controlled temperature room set at about 10-12°C (50-54°F). Four VOCs were used: methylene chloride, chloroform, 1,2-dichloroethane, and toluene (Mix 1 from Table 8). These were injected in 2 mL of methanol solution containing from 1.64-4.68 mg/L of each VOC, resulting in about 120 mL aqueous solution with concentrations ranging from 27.3-78.0 µg/mL of each VOC. Each experiment was run at least in duplicate for a one-hour and an 18-hour period. The concentration of each VOC in vppm was divided by the concentration of the control (no membrane) to yield a value of percent permeation. The vppm values were not related to expected Henry's law constant values, since the experiment was designed to measure permeation across the membranes only (Table 11). For actual measurements of VOC concentrations in water samples, some additional means of agitation would be needed.

**Table 11. Permeation Across Membranes from Headspace Above Water and from Water Surface at 10-12°C (50-54°F)**

	<u>Percent Permeation</u>			
	Methylene Chloride	Chloroform	1,2- Dichloroethane	Toluene
<u>0.025 mm PE</u>				
1 Hour				
Upright	32,37	35,30	38,31	93,83
Inverted	25,23	28,26	27,26	61,61
18 Hour				
Upright	70,86	69,82	83,86	91,94
Inverted	82,69,75	85,67,71	84,62,68	103,65,73
<u>0.254 mm Poly(siloxane)</u>				
1 Hour				
Upright	93,86	78,69	67,67	36,31
Inverted	72,71	59,58	54,56	23,25
18 Hour				
Upright	105,115	90,86	92,83	45,36
Inverted	130,107	99,83	90,70	48,30



**Table 11., continued**

	<u>Percent Permeation</u>			
	Methylene Chloride	Chloroform	1,2- Dichloroethane	Toluene
<u>0.02<math>\mu</math> pore size PTFE</u>				
1 Hour				
Upright	93,113	97,113	89,115	101,114
Inverted	51,36	51,37	50,36	51,37
18 Hour				
Inverted	77,75	81,74	68,66	81,74
10 Minutes				
Upright	106	105	108	104
<u>0.025 mm PE 0.2<math>\mu</math> pore size PTFE</u> (backing screen removed)				
1 Hour				
Upright	96	93	102	98
Inverted	42	41	42	44
18 Hours				
Inverted	73	77	68	73

The results show that PTFE passed all four standards completely in one hour in the upright configuration (air contacting the membrane). The passage of VOC vapors is not complete at one hour for the non-porous membranes but is nearly complete at 18 hours for some of the VOCs. Another experiment showed that of VOCs through the porous PTFE was complete in 10 minutes. Thus, it appears that the PTFE does not provide any significant barrier to VOC passage when compared to the same configuration with no membrane present. For all three membranes, the passage of VOCs was more rapid for the upright (air contacting the membrane) than for the inverted (water contacting the membrane) positions. For the nonporous membranes, there appears to be some selectivity between the aromatic and chlorinated compounds. After 18 hours, PE passes toluene completely, but not the chlorinated compounds, while the opposite occurs with poly(siloxane). The behavior of a 0.2 $\mu$  porous PTFE membrane (with polypropylene screen backing removed) is

essentially identical to the 0.02 $\mu$  porous membrane (Table 11), indicating that in this pore size range, the non-polar nature of PTFE rather than the pore size controls its behavior.

The results imply that a porous PTFE membrane is suitable for protecting a sensor from liquid water if there is some air above the water level in contact with the membrane. If the membrane is in full contact with the water on one side, the exchange of VOCs is slowed significantly. The transport from air through porous PTFE is rapid, which is a necessary condition for rapid, short term measurements. For longer term monitoring, the non-porous PE or poly(siloxane) membranes could be useful in protecting a sensor. The chemical selectivity exhibited by these latter two membranes possibly could be used to advantage for selective monitoring of specific VOC chemical classes.

## CONCLUSIONS

The results of this study show that it is possible to measure toluene to a level near 1 vppm with a down hole PID sensor device with a 0.25 mA lamp current. This corresponds to a headspace level above a 14  $\mu$ g/L (ppb) toluene solution in water at 25°C (77°F). Thus, a device which maintains a headspace above the water level could be used for subsurface analysis and monitoring applications. A value for  $H_i$  represents an ideal condition at infinite dilution for a particular temperature. Thus, a single  $H_i$  value for a particular VOC such as toluene can provide only an approximation of concentration in the field. The data show that conditions resulting in apparent, practical deviations from Henry's law include temperature and VOC concentration.

Studies with membranes show that membranes which allow passage of VOCs also allow some passage of water vapor. A membrane could play a useful role in protecting the sensor from direct contact with liquid water down hole. The porous PTFE membrane allows for a rapid passage of VOCs for rapid measurements, while the 0.254 mm poly (siloxane) membrane seems to have the least water vapor permeation for possible long term monitoring. The rate of diffusion to the sensor might be a limiting factor for rapid measurements. Various means of mixing may need to be considered.

## REFERENCES

- Anheier, N.C., K.B. Olsen, R.E. Osantowski, J. C. Evans, Jr., and J.W. Griffin, 1993, Fiber-Optic Spectrochemical Emission Sensor: Detection of Volatile Organic Chlorinated Compounds in Air and Water Using Ultra-thin Membranes, *Proc. Electrochem. Soc., Symposium on Chemical Sensors*, 93-7.
- Dean, J.A. ed., 1973, *Lange's Handbook of Chemistry*. McGraw-Hill, New York, NY.
- Dewulf, J., D. Drijvers, and H. Van Langenhove, 1995, Measurement of Henry's Law Constant as a Function of Temperature and Salinity for the Low Temperature Range, *Atmospheric Environment*, 29(3), 323-331.
- Dreisbach, R., 1961, Physical Properties of Chemical Compounds, *in Advances in Chemistry*, No. 29, American Chemical Society Press, Washington, D.C.
- Driscoll, J.N., J.H. Becker, 1979, Industrial Hygiene Monitoring with a Variable Selectivity Photoionization Detector, *American Laboratory*, 11 (11): 101-110.
- Greenwalt, C.C., K.J.Voorhees, and J.H. Futrell, 1983, Transmission of Organic Molecules by Silicone Membrane Gas Chromatograph/Mass Spectrometer Interface, *Analytical Chemistry*, 55, 468-472.
- Hoch, G., and B. Kok, 1963, A Mass Spectrometer Inlet System for Sampling Gases Dissolved in Liquid Phases, *Archives of Biochemistry and Biophysics*, 101, 160-170.
- Kerndorff, H., R.H. Plumb, R. Schleyer, and G. Milde, 1992, Anthropogeochemistry of Groundwater Pollutants from Waste Sites, *in Lesage, S. and R.E. Jackson, eds., Groundwater Contamination and Analysis at Hazardous Waste Sites*. Marcel Dekker, New York, NY, 245-271.
- Langhorst, M.L., 1981, Photoionization Detector Sensitivity of Organic Compounds, *Journal of Chromatographic Science*, 19, 98-103.
- Le Goullon, D. and K. Goswami, 1990, Fiber Optic Refractive Index Sensor Using a Metal Clad. U.S. Patent 4,929,049.
- Mackay, D. and T.K. Yeun, 1983, Mass Transfer Coefficient Correlations for Volatization of Organic Solutes from Water, *Environmental Science and Technology*, American Chemical Society, Washington, D.C., 17, 211-217.

- Milanovich, F.P., D.G. Garvis, S.M. Angel, S.M. Klainer, and L. Eccles, 1986, Remote Detection of Organochlorides with a Fiber optic Sensor. *Analytical Instrumentation*, 15, 137-147.
- Nielsen, F., E. Olsen, and A. Fredenslund, 1994, Henry's Law Constants and Infinite Dilution Activity Coefficients for Volatile Organic Compounds in Water by a Validated Batch Air Stripping Method, *Environmental Science and Technology*, 28, 2133-2138.
- Olsen, K.B., J.W. Griffin, D.A. Nelson, B.S. Matson, and P.A. Esbach, 1989, Prototype Design and Testing of Two Fiber Optic Spectrochemical Emission Sensors. *Proc. First Annual Field Screening Methods for Hazardous Waste Site Investigations*, Las Vegas, NV, USEPA EPA/600/D-89/189.
- Oxenford, J.L., S. M. Klainer, T.M. Salinas, L. Todechney, J.A. Kennedy, D.K. Dange, and K. Goswami, 1989, Development of a Fiber Optic Chemical Sensor for the Monitoring of Trichloroethylene in Drinking Water. *SPIE Proceedings*, Boston, MA, 108-114.
- Plumb, R.H.Jr., 1992, The Importance of Volatile Organic Compounds as a Disposal Site Monitoring Parameter, in Lesage, S. and R.E. Jackson, eds., *Groundwater Contamination and Analysis at Hazardous Waste Sites*. Marcel Dekker, New York, NY, 173-197.
- Plumb, R.H.Jr., 1991, The Occurrence of Appendix IX Organic Constituents in Disposal Site Ground Water, *Ground Water Monitoring Review*, 11 (2): 157-164.
- Snyder, L.R., *Principles of Adsorption Chromatography*. Marcel Dekker, New York, NY, 206-210.
- Stetter, R.S., and Z. Cao, 1990, Gas Sensor and Permeation Apparatus for the Determination of Chlorinated Hydrocarbons in Water, *Analytical Chemistry*, 62, 182-185.
- Strike, D.J., P. Arquant, N.F. de Rooij, and M.Koudelka-Hep, 1993, Spatially Controlled Membrane Depositions for Silicon-Based Sensors, *Chimia* 47, 241-244.
- van der Leeden, F., F.L. Troise, and D.K. Todd, 1990, *The Water Encyclopedia*, second edition, Lewis Publishers, Michigan, 252.
- Weast, R.C., M.J. Astle, and W.H. Beyer, eds., 1971, *CRC Handbook of Chemistry and Physics*. CRC Press, Inc., Boca Raton, FL.