

FIELD SCREENING FOR HALOGENATED VOLATILE ORGANIC COMPOUNDS

Topical Report

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ABSTRACT

Western Research Institute (WRI) initiated exploratory work towards the development of new field screening methodology and a test kit to measure halogenated volatile organic compounds (VOCs) in the field. Heated diode and corona discharge sensors are commonly used to detect leaks of refrigerants from air conditioners, freezers, and refrigerators. They are both selective to the presence of carbon-halogen bonds. Commercially available heated diode and corona discharge leak detectors were procured and evaluated for halogenated VOC response. The units were modified to provide a digital readout of signal related to VOC concentration. Sensor response was evaluated with carbon tetrachloride and tetrachloroethylene (perchloroethylene, PCE), which represent halogenated VOCs with and without double bonds. The response characteristics were determined for the VOCs directly in headspace in Tedlar bag containers. Quantitation limits in air were estimated. Potential interferences from volatile hydrocarbons, such as toluene and heptane, were evaluated. The effect of humidity was studied also. The performance of the new devices was evaluated in the laboratory by spiking soil samples and monitoring headspace for halogenated VOCs. A draft concept of the steps for a new analytical method was outlined. The results of the first year effort show that both devices show potential utility for future analytical method development work towards the goal of developing a portable test kit for screening halogenated VOCs in the field.

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EXECUTIVE SUMMARY

Western Research Institute (WRI) initiated exploratory work towards the development of new field screening methodology and a test kit to measure halogenated volatile organic compounds (VOCs) in the field. Heated diode and corona discharge sensors are commonly used to detect leaks of refrigerants from air conditioners, freezers, and refrigerators. They are both selective to the presence of carbon-halogen bonds. Commercially available heated diode and corona discharge leak detectors were evaluated for halogenated VOC response. The units were modified as necessary to provide a numerical readout of signal related to VOC concentration. Sensor response was evaluated with carbon tetrachloride and tetrachloroethylene (perchloroethylene, PCE), which represent halogenated VOCs with and without double bonds. The response characteristics were determined for the VOCs directly in headspace in Tedlar bag containers. Detection limits in air were estimated. Potential interferences from volatile hydrocarbons, such as toluene and heptane, were evaluated. The effect of humidity was studied also. The performance of the new devices was evaluated in the laboratory by spiking soil samples and monitoring headspace for halogenated VOCs. A draft concept of the steps for a new analytical method was outlined. A summary of accomplishments from the current FY 01 effort is listed below.

- Commercially available heated diode and corona discharge leak detectors were obtained from the manufacturers. These were modified as required to provide readouts that correspond to the concentration of halogenated VOCs in air.
- Sensor response was evaluated by isolating variables such as VOC type and potential interferences. Responses were evaluated in air for two distinctly different types of halogenated VOCs; one without double bonds, carbon tetrachloride; and one with a double bond, tetrachloroethylene. The response characteristics were determined for the VOCs directly in headspace, without soil, in containers such as Tedlar bags. Quantitation limits (S/N=10) were estimated to be 0.2 vppm for the heated diode detector and 10 vppm for the corona discharge detectors. Potential interferences from volatile hydrocarbons, such as toluene and heptane, were evaluated and found to be minimal. The effect of humidity was studied also. Humidity did not affect the response profiles of either detector to carbon tetrachloride. Minimal backgrounds due to saturated humidity could easily be zeroed out.
- The performance of the new devices was evaluated in the laboratory by spiking soil samples and monitoring headspace for halogenated VOCs. A draft concept of the steps required to develop new analytical methods with these devices was prepared.

OBJECTIVES

The ultimate goal of the multiyear effort is to develop a field portable kit based on heated diode or corona discharge monitor technology for screening halogenated volatile organic compounds (VOCs) in the field. The objectives of the first-year effort were to obtain two widely used commercially available refrigerant leak detectors and evaluate them for possible use as field screening and monitoring devices for halogenated VOCs. Heated diode leak monitors are commercially available from Yokogawa U.S. Corporation in Newnan, Georgia. These operate on 12 or 120 volts at less than 1 amp. Corona discharge leak monitors are commercially available from American Test Products Inc., Miami, Florida. These involve high-impedance circuits operating at about 1,600 volts at the detector tip. Both types of sensor systems are said to be able to detect leaks of down to about 0.1 to 0.5 ounce of refrigerant per year. Both of these detectors are sold as alarm monitors without a digital readout. Western Research Institute (WRI) modified both of these types of commercially available monitors to provide quantitative or semiquantitative determination of halogenated VOCs in the field. Initial experiments were performed with carbon tetrachloride and tetrachloroethylene in air and soil. The concept of a new analytical method was established.

INTRODUCTION

Halogenated Volatile Organic Compounds

Contamination by halogenated VOCs is a widespread problem at U.S. Department of Energy (DOE) and military sites. Compounds such as carbon tetrachloride, trichloroethylene, tetrachloroethylene, etc. are commonly referred to as dense nonaqueous phase liquids (DNAPLs). These were used extensively in degreasing and equipment cleaning operations in the past, with disposal practices that led to their release into the ground. Some are still in use as degreasing solvents in the petroleum refining and other industries (U.S. DOE 1998). Studies of data from 500 sites show that VOCs are the most significant organic contaminants in groundwater associated with disposal sites (Plumb 1992). These represented 75% of events involving organic contamination in both CERCLA, RCRA, and municipal landfill sites. Plumb (1992) found an identical mathematical relationship between VOCs and organic priority pollutants detected. He suggested 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 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).

Background

A new screening method was developed by WRI for determining the presence of fuels containing aromatic components, particularly diesel fuel in soils (Sorini and Schabron 1997, Schabron et al. 1995). It has been approved by the American Society for Testing and Materials

(ASTM) as Method D-5831, Standard Test Method for Screening Fuels in Soils (ASTM 2000).

Table 1. PID Detectability for Volatile Organic Compounds

| <u>Compound</u> | PID Detectability | |
|---|-------------------|---------------|
| | <u>10.6eV</u> | <u>11.7eV</u> |
| Dichloromethane (Methylene chloride) | N | Y |
| Trichloroethylene | Y | Y |
| Tetrachloroethylene | Y | Y |
| trans-1,2-Dichloroethene | Y | Y |
| Trichloromethane (Chloroform) | N | Y |
| 1,1-Dichloroethane | N | Y |
| 1,1-Dichloroethene | Y | Y |
| 1,1,1-Trichloroethane | N | Y |
| Toluene | Y | Y |
| 1,2-Dichloroethane | N | Y |
| Benzene | Y | Y |
| o-Xylene | Y | Y |
| Ethylbenzene | Y | Y |
| Vinyl chloride | Y | Y |
| Carbon tetrachloride | N | Y |
| Chlorobenzene | Y | Y |
| p-Dichlorobenzene | Y | Y |
| Naphthalene | Y | Y |

A new *Diesel Dog*[®] Soil Test Kit is being commercialized by WRI to perform the method in the field. Questions frequently arise as to whether the kit can measure volatile DNAPLs, since this is a problem encountered by many state agencies and environmental engineering firms. The method employed by the *Diesel Dog* kits measures aromatic rings by ultraviolet light absorption, thus it is not amenable to halogenated VOCs. A need for a simple portable field kit and method to detect volatile DNAPLs is apparent. Over the last decade, research at WRI included work with photoionization detection (PID) with various types of VOCs in soil and water. PID is the most common VOC field screening tool in use today. A typical PID lamp energy is 10.6 electron volts (eV), which is sufficient for ionizing compounds containing double bonds. However, halogenated compounds without double bonds, such as carbon tetrachloride or methylene chloride, require an energy of 11.7 eV for ionization (Table 1) (Driscoll and Becker 1979). This can only be

accomplished with a PID equipped with a lithium fluoride window, which has a short lifetime due to the solubility of lithium fluoride in water. Also, a PID is not selective for halogenated compounds. Many other compound types are detected also. Field screening with a PID probe involves placing a soil sample in a plastic bag or a glass jar, sealing the bag or covering the jar with aluminum foil, then inserting the PID probe tip through the foil (Hewitt and Lukash 1997).

There exists a need for a new type of simple field monitor that is selective to halogenated VOCs. Heated diode and corona discharge sensors are commonly used as alarm monitors to detect leaks of refrigerants from air conditioners, freezers, and refrigerators. Both are selective to the presence of carbon-halogen bonds. The expertise that has been developed at WRI in the area of field test kits and the measurement of VOCs is being applied to developing a new environmental monitoring application for heated diode or corona discharge-based leak detectors. This is expected to result in a new method and test kit for selectively screening for halogenated VOCs in the field. The devices could be used with the plastic bag or foil-covered jar sampling procedures described above for soil samples, or to measure the headspace above water.

Recent research at WRI involved studies of the partitioning of VOCs between air and water as a function of temperature and the concentration of VOC species in water (Schabron et al. 1996, Schabron and Rovani 1997). Headspace can be either in the air above the water table in a well, or artificially created below the surface of the water by a membrane or other device. The principle of operation for a 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 :

$$P_i = H_i \times C_i \quad (1)$$

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. For example, H_i relates the mg/L vapor 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, field screening personnel often assume that the aqueous level can be established. H_i is only defined at infinite dilution and the partitioning varies significantly with total VOC water concentration and with temperature (Schabron and Rovani 1997). Headspace can only be used to estimate water concentration if the appropriate corrections can be made.

Current Approaches

The most common instruments used for field screening for VOCs are hand-held PID-based

instruments. PID detectors suffer from a disadvantage in that they cannot discriminate between halogenated and non-halogenated species (Table 1). A more detailed analysis that also allows for some speciation involves a portable gas chromatograph (Myers et al. 1995, Linenberg 1995). Skilled operators are required. Immunoassay kits allow for rapid field analysis (Hudak et al. 1995). This approach requires temperature control and critical timing for the several steps involved.

Several novel approaches have been proposed for surface or down-hole screening of halogenated VOCs in the field (Schabron et al. 1991). One approach uses refractive index attenuation on coated optical fibers (Le Goullon and Goswami 1990, Oxenford et al. 1989). Another technology uses a chemical reaction in a basic media to form a color in the presence of trichloroethylene (Milanovich et al. 1994, 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 LaF_3 -doped element heated to 600 °C (1,112 °F) to measure volatile chlorine-containing compounds (Buttner et al. 1995, Stetter and Cao 1990). A synthetic nose consisting of an array of different chemicals that give different optical response to various volatile analytes has been proposed (Walt 1998). Other approaches include Raman spectroscopy (Ewing et al. 1995, Haas et al. 1995), electrochemical cells (Adams et al. 1997), acoustic wave devices (Frye et al. 1995), and ion mobility spectrometry (Stach et al. 1995). The above devices all contribute some progress towards the problem of monitoring for some of the VOC indicator compounds at various levels. These are not commercially available.

The detector system also must 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. Potential interferences from aliphatic or aromatic hydrocarbons must be minimal. The detector must demonstrate a significant selectivity to halogenated VOCs in the presence of non-halogenated VOCs.

New Methodology

The current work is expected to lead to the development of new commercial products that will provide a cost-effective means to rapidly screen for halogenated VOCs in the field. The work involves taking existing refrigerant detector alarm monitors, and with slight hardware modification and comprehensive analytical method development, launching them into a new commercial application with significant utility to the environmental industry. The ultimate goal of the multiyear effort is to develop a field portable kit based on heated diode or corona discharge monitor technology for screening for halogenated VOCs in the field. The objectives of the proposed work are to obtain two widely used commercially available refrigerant leak detectors and evaluate them for possible use as field screening and monitoring devices for halogenated VOCs. Heated diode leak monitors are commercially available from Yokogawa U.S. Corporation in Newnan, Georgia. These operate on 12 volts at less than 1 amp. Corona discharge leak monitors are commercially available from TIF Instruments, Inc., Miami, Florida. These involve high-impedance circuits operating at

about 1,600 volts at the detector tip. Both types of sensor systems are said to be able to detect leaks of down to about 0.1 to 0.5 ounce of refrigerant per year. Both of these detectors are sold as alarm monitors without a digital readout.

EXPERIMENTAL DETAILS

Chemicals

Carbon tetrachloride and tetrachloroethylene (perchloroethylene, PCE) were 99% + from Aldrich. Heptane and toluene were reagent grade from commercially available sources.

Heated Diode Leak Detector

The heated diode sensor was a model H-10PM refrigerant leak detector from Yokogawa Corporation, Newnan, Georgia.

Corona Discharge Leak Detectors

The corona discharge devices were the TIF model XP-1 and the TIF H-10A refrigerant leak detectors from Advanced Test Products, Inc., Miami, Florida.

Gas Chromatography

The gas chromatography (GC) analyses were performed with a Hewlett-Packard 5890A GC equipped with an electron capture detector. The column was a J&W DB-624 30 m x 0.53 mm i.d. x 3 micron film thickness. Six GC calibration standards for each VOC were prepared from certified standard solutions in methanol from Supelco. Volume amounts of 1 uL of each of the six calibration standards were injected into the GC, and a linear calibration range consisting of area response vs. pg of VOC injected was determined on a daily basis.

Tedlar Bag Experiments

Saturated headspace vapors of carbon tetrachloride and tetrachloroethylene were obtained by pipetting 20 mL of liquid-phase VOC into a 175-mL, glass, gas-sampling apparatus containing a PTFE-lined silicone septum. After overnight liquid/vapor equilibration, the ambient laboratory air temperature was recorded, and various uL quantities of saturated headspace vapor were withdrawn through the septum using a gas-tight syringe. These were injected into septum-ported 1-L and 5-L Tedlar bags containing dry breathing-quality grade air introduced from a gas cylinder. Vapor equilibration by diffusion was found to take only a few minutes, and various uL quantities of air containing VOC vapor were withdrawn from the Tedlar bags by gas-tight syringes and injected into the GC for analysis to determine vppm concentrations.

The probe tip of the Yokogawa H-10PM was inserted into the Tedlar bag port, after quickly removing the septum. The on-board air pump was used to draw sampled air into the heated diode chamber. The heated diode sensor response in volts was recorded using the strip chart recorder wired to the amplified signal outputs. Signal responses ranging from 0 through 15 volts were recorded for the small, medium, and large settings, using the unit's auto mode. Between individual Tedlar bag readings, the unit was rezeroed using a bag blank containing dry air only.

The probe tip of the TIF XP-1 was inserted into the bottom port of a carefully machined 316 stainless steel "T" fitting. A two-inch piece of PTFE tubing was used to connect one of the top ports to a Du Pont P200A personal sampling pump set at a flow rate of 150 mL/min. A second two-inch piece of PTFE tubing was used to connect the other top port of the "T" to the Tedlar bag port, after quickly removing the septum. The corona discharge responses were recorded by counting the number of LED lights illuminated at sensitivity levels 1 through 5. Between individual Tedlar bag readings, the unit was rezeroed using a bag blank containing dry air only.

The probe tip of the TIF H-10A was inserted directly in the Tedlar bag port, and a small fan located just downstream from the corona discharge sensor pulled sampled air past the sensor. The frequency of the audible signal response was recorded using a multimeter set to the frequency (Hz) mode. Frequency responses were obtained at three sensitivity levels, using blank background settings at 1, 2, and 4 Hz. Between individual Tedlar bag readings, the unit was rezeroed using a Tedlar bag blank containing dry air only.

Water Vapor Experiments

The H-10PM and XP-1 were tested for their response to saturated water vapor at ambient temperatures. 1 mL of water was pipetted into a 1-L Tedlar bag, and the bag was manually shaken. After overnight liquid/vapor equilibration, the units were set to zero with dry air and evaluated for their response to 100% relative humidity.

In similar fashion to the dry air environment experiments described above, carbon tetrachloride vapor responses were obtained in saturated water vapor environments, using 1 mL of water pipetted into a 1-L Tedlar bag, and 5 mL of water pipetted into a 5-L bag. After overnight liquid/vapor equilibration at ambient laboratory temperatures, carbon tetrachloride vapor concentrations in the presence of 100% relative humidity were determined by GC, and the responses were obtained for the heated diode H-10PM and the corona discharge XP-1 devices. Between individual Tedlar bag readings, the units were rezeroed using a Tedlar bag blank containing dry air only. A second set of responses was obtained in which the units were rezeroed using a Tedlar bag blank containing saturated water vapor.

Toluene and n-Heptane Vapor Experiments

The H-10PM and XP-1 were tested for their response to toluene and n-heptane vapors. Saturated headspace vapors of toluene and n-heptane were prepared in glass, gas-sampling apparatuses as described above. Various volumes of saturated headspace vapor were withdrawn and injected into Tedlar bags containing dry air, and the units were evaluated for their response.

The H-10PM and XP-1 were then evaluated for their response to carbon tetrachloride vapor in the presence of toluene vapor and n-heptane vapor environments. For these studies, volumes of toluene and n-heptane vapor equal to the carbon tetrachloride vapor volume, 10 times the carbon tetrachloride vapor volume, and 100 times the carbon tetrachloride vapor volume were added to Tedlar bags. Between individual Tedlar bag readings, the units were rezeroed using a Tedlar bag blank containing dry air only. A second set of responses was obtained in which the units were rezeroed using a Tedlar bag blank containing the appropriate volume of toluene or n-heptane vapor environment in which the carbon tetrachloride response was being evaluated.

Soil Spiking

The H-10PM and XP-1 units were evaluated for their response to carbon tetrachloride spiked into soil contained inside the Tedlar bags. These experiments were used to compare VOC in soil concentrations (mg VOC/Kg soil) with VOC in air concentrations (vppm).

Sensor Interchangeability

All three units were evaluated for replacement sensor interchangeability. Carbon tetrachloride vapor responses were obtained for five sensors for the H-10PM and the H-10A and for four sensors for the XP-1. Since the sensor response of the H-10PM heated diode sensor can be altered via temperature adjustment, studies were conducted to see if the five individual sensors could be “tuned” to produce similar response profiles.

RESULTS AND DISCUSSION

Sensor Response

Sensor response was evaluated by isolating variables such as VOC type and potential interferences. Responses were evaluated for two distinctly different types of halogenated VOCs; one without double bonds, carbon tetrachloride; and one with a double bond, tetrachloroethylene. The response characteristics were determined for the VOCs directly in

headspace, without soil, in containers such as Tedlar bags. Quantitation limits were estimated based on a signal to noise ratio of 10. Potential interferences from volatile hydrocarbons, such as toluene and heptane, were evaluated. The effect of humidity was studied also.

Yokogawa Heated Diode Sensor

Model H-10PM Description

The heated diode sensor was a model H-10PM refrigerant leak detector from Yokogawa Corporation, Newnan, Georgia (Figure 1). The diode is heated between temperatures ranging from about 600–1,000 °C (1,112–1,832 °F). It selectively interacts with halogens present in the volatile organic compounds that it encounters. This is based on positive ion emission technology, wherein halogens cause an ionized current to flow. The device has an on-board sampling pump that operates at two flow rates that control the device's sensitivity. The low flow rate provides the most sensitivity, while the highest flow rate provides the least sensitivity. Sensitivity can also be controlled by adjusting the temperature of the diode heater, with a higher temperature providing greater sensitivity. There is an audio alarm with a chirping sound that is indicative of the amount of volatile halogenated compounds present. Since there is no visual readout, the device was modified according to instructions from the manufacturer by CF Electronics, Laramie, Wyoming, to provide an output signal that ranges from 0 to 15 V. The output was connected to a Linseis L200E strip chart recorder.

The H-10PM has an autozero function that provides steady readings when the unit is in this mode. It also has three sensitivity settings; small, medium, and large. The small setting provides the most sensitivity. The settings alter the amplified signal by changing the air flow rate to the detector, and by electronic attenuation. The small setting uses a pump flow rate of 110 mL/min, while the medium and high settings use a pump flow rate of 160 mL/min.

The H-10PM also has a sensor temperature adjustment that must be used to periodically adjust the sensor response when a reading is made by diffusion from a small vial containing a sample of refrigerant provided by the manufacturer. Over time, the sensor begins to lose its sensitivity. A temperature adjustment restores its response profile to its former state to give responses similar to earlier measurements. Eventually, the diode is spent and it must be replaced with a new one.

Carbon Tetrachloride

Figure 2 shows the response profile of the H-10PM to carbon tetrachloride vapor in dry air for each of the unit's three settings. The profile for the large setting is the most comprehensive, but also the most non-linear. The unit's response has approached an upper range limit of about 80 vppm where the heated diode response has maximized on the large setting.

Figure 3 is an expanded view of the lower working range of the unit, and illustrates the region from near the detection limit up to 5 vppm carbon tetrachloride. A detection limit of 0.2 vppm was calculated with the strip chart recorder using a signal to noise ratio of 10 on the small setting. Note that the linear range of the small setting is rather narrow, from 0.2 to about 1 vppm.

Water Vapor

The H-10PM was evaluated for its response to water vapor. The response of the unit on the small setting to saturated water vapor at 25 °C (77 °F) was found to be equivalent to about 0.095 vppm carbon tetrachloride in dry air. Likewise, the medium setting yielded 0.092 vppm, and the large setting produced a response equivalent to 0.014 vppm. Although the unit does exhibit a slight response to 100% relative humidity, the presence of water vapor can be considered insignificant for two reasons. First, the response profile of carbon tetrachloride vapor in the presence of saturated water vapor (Figure 4) is almost identical to that in dry air (Figure 3). Second, proper use of the unit as an analytical tool would require that it be periodically rezeroed, which could simply be performed in the ambient humid air background. This would serve to effectively cancel out the small contribution of humidity in the response.

Toluene and n-Heptane Response

The response of the H-10PM to toluene vapor is minimal, as shown as Figure 5. Note that all of the responses for the three settings are below 0.2 volts on the Y axis, compared to a high of 15 volts previously found to define the upper range of the three settings. The large setting, in particular, produces almost no response to toluene vapor. In addition, Figure 6 demonstrates that the presence of toluene vapor does not significantly alter the response profile of the heated diode to carbon tetrachloride vapor (as compared with Figure 3). Actual volumes of toluene used for these experiments were a volume equal to that of carbon tetrachloride, 10 times that of carbon tetrachloride, and 100 times that of carbon tetrachloride. These volumes represent toluene vppm concentrations of 0.25, 2.5, and 25 times that of carbon tetrachloride vppm concentrations, based on relative vapor pressures at ambient temperature.

The response of the H-10PM to n-heptane vapor is also minimal, as shown in Figure 7. As with toluene, all three settings produce responses less than 0.2 volts, and the large setting produces essentially no response. Figure 8 demonstrates that the presence of n-heptane vapor does not significantly alter the response profile of the heated diode to carbon tetrachloride vapor, and is almost identical to Figure 3. Actual volumes of n-heptane used were a volume equal to that of carbon tetrachloride, 10 times that of carbon tetrachloride, and 100 times that of carbon tetrachloride. These volumes represent n-heptane vppm concentrations of 0.4, 4.0, and 40 times that of carbon tetrachloride vppm concentrations, based on relative vapor pressures at ambient temperature.

Sensor Interchangeability and Tuning

At this point in the study, it was observed that the original sensor diode (sensor #1) was starting to give inconsistent results when compared to previous data. The temperature of the sensor was changed in several attempts to restore it to original performance. This proved unattainable, suggesting that the sensor was spent and therefore, required replacement. Four replacement sensor diodes (#2 through #5) were subsequently evaluated using carbon tetrachloride vapor. Figure 9 shows the variability between sensors #2 through #5 at identical temperature settings. Based on these data, experiments were then conducted to “tune” the sensors to give similar response profiles. Raising the temperature of the sensors made them more sensitive (and vice versa), and Figure 10 shows that sensors #2 through #5 could indeed be tuned to yield similar response profiles. However, at higher vppm concentrations, the tuned response profiles of the replacement sensors were found to be significantly different from the response profile of original sensor #1. It is unclear whether this is indicative of an electronic problem related to long-term unit operation, or simply random variation between experiments conducted months apart.

Soil Spiking

Sensor #2 was employed for the soil spiking study, using a riverbank soil obtained locally. One-gram portions of soil were weighed into individual Tedlar bags, and various concentrations of carbon tetrachloride in a 100-uL methanol aliquot were added to the soil by micropipette. The bags were immediately sealed, and the contents were shaken and allowed to equilibrate overnight. For comparison purposes, aliquots were also spiked into empty Tedlar bags containing no soil. The results of the spiking studies are shown in Figure 11. The slight variation between the empty bag (w/o) and soil spike (w) results is probably due to experimental error, because a subsequent study yielded similar results, but with opposite effect in which the soil spikes produced less response than the empty bag. Of particular interest is the relationship between the spiked mg VOC/Kg soil concentrations and vppm results. This correlation is influenced by the volume of the Tedlar bag (~ 1-L volume), and implies that a lower detection limit and quantitation range can be achieved by decreasing the headspace volume. A hypothetical field method using 2.5 g of soil and 50-mL headspace volume suggests that a 50-fold increase in the detection limit and quantitation range for soil relative to air can be achieved.

Tetrachloroethylene

Relative sensitivities of the heated diode system were measured with a single diode at low, medium, and high sensitivity settings at low, medium, and high concentrations of both carbon tetrachloride and tetrachloroethylene (PCE). The data are presented in Table 2. The response to PCE on the high sensitivity setting was only about 0.42 V, which appears to be near a threshold value for the device. The results for the medium and high sensitivity settings show

that the response to tetrachloroethylene is on average only 23% of the response to carbon tetrachloride. Both of these VOCs contain four chlorine atoms. PCE has a double bond. Apparently, the differences between these compounds causes a different reaction with the heated diode that results in different sensitivities.

Table 2. Yokogawa H-10PM Relative Response of Carbon Tetrachloride and Tetrachloroethylene

| <u>Sensitivity</u> | <u>Instrument Setting</u> | <u>Concentration CCl₄, vppm</u> | <u>Response V/vppm</u> | <u>Concentration PCE, vppm</u> | <u>Response V/vppm</u> | <u>Response PCE/CCl₄</u> |
|--------------------------------|---------------------------|--|------------------------|--------------------------------|------------------------|-------------------------------------|
| High | Small | 3.50 | 2.4 | 2.04 | 0.21 | 0.09 |
| Medium | Medium | 14.4 | 0.90 | 11.2 | 0.19 | 0.21 |
| Low | Large | 32.5 | 0.24 | 29.8 | 0.06 | <u>0.25</u> |
| Average (medium and low): 0.23 | | | | | | |

TIF Corona Discharge Sensors

Model XP-1 Description

The corona discharge device with which the initial experimental work was performed was a TIF model XP-1 refrigerant leak detector from ATP, Inc., Miami, Florida (Figure 12). The sensor tip operates at a potential difference of 1,500 to 2,000 VDC. A discharge current of about 10 microamperes is decreased by the presence of halogen-containing VOCs. This perturbation of current is difficult to interpret directly, and the manufacturer has developed a digital signal processing algorithm to convert the change in current and voltage into an audible alarm and a

visual readout consisting of a series of lighted diodes on the front panel that relate to the concentration of contaminant.

The TIF XP-1 contains a small fan located within the body of the unit that is designed to pull sampled air past the probe tip and through a flexible wand. However, no air flow could be detected at the sensor tip. Subsequent disassembly showed that the fan, either by design or ineffective sealing, was not capable of pulling sampled air through the wand and past the sensor tip. To circumvent this problem, the unit was modified to deliver a constant flow of sampled air past the sensor tip. The pump chosen for this purpose is an air sampling pump usually employed for precise chemical vapor air monitoring in personal hygiene applications. The pump was configured to pull sampled air past the sensor tip upstream from the pump. The sensor tip was fitted into a low-void volume 316 stainless steel “T” carefully machined to eliminate leakage and void volumes, and to provide consistent air flow past the sensor tip. Different pump air flows were initially explored, and a flow rate of 150 mL/min was chosen.

The XP-1 produces an audible beep and an LED readout when chemical vapors are detected. The frequency of the beep, and the color and number of LED lights is proportional to the amount of chemical vapor detected. At the request of WRI, the model XP-1 was custom configured by the manufacturer with two wire leads to the corona discharge detector. The signals produced by these leads were found to be inconsistent. In some instances the wire leads were found to adversely affect the detector by creating artificial signals. The audible beep cannot be used to quantitate or estimate amounts or concentrations of chemical vapors. However, the LED readout can be employed in a somewhat simple fashion to gauge the approximate concentration of chemical vapors. The LED readout of three colors and six lights produces a net signal range of 0 through 18 lights for each of the unit’s seven sensitivity levels. The levels electronically attenuate the signal from the corona discharge detector; level 7 is the most sensitive while level 1 is the least sensitive. Sensitivity level 7 and to a lesser degree, 6, could not be used reliably in this study because they were found to give irreproducible and inconsistent results. Reliable signals in laboratory experimentation were generated for levels 1 through 5. For the study, the number of lights was determined by visual means. To reliably employ this device as a quantitative analyzer, a more precise electronic readout would have to be developed.

Carbon Tetrachloride

Figure 13 shows the response profile of the XP-1 to carbon tetrachloride vapor in dry air for each of the unit’s five sensitivity levels tested. Maximum responses are reached for levels 3, 4, and 5 at about 1,000 vppm, where it appears that the sensor has become saturated. Figure 14 is an expanded view of the lower working range of the XP-1, and illustrates the region near the detection limit up to about 40 vppm carbon tetrachloride. Using the level 5 setting, a detection

limit of approximately 10 vppm can be obtained using the least number of lights that yield a reliable result, which is estimated to be either two or three lights.

Water Vapor

The TIF XP-1 gives a somewhat pronounced chemical response to saturated water vapor in air at ambient temperature, which is equivalent to approximately 20 vppm of carbon tetrachloride using the level 4 and 5 settings. Thus, the response curve of carbon tetrachloride vapor in combination with 100% relative humidity is the combined sum of the two individual responses. However, as shown in Figure 15, if the XP-1 is rezeroed in the 100% relative humidity environment, the response curve of carbon tetrachloride vapor in combination with saturated water vapor is within experimental error to that of carbon tetrachloride in dry air (Figure 14). Thus, proper use of the unit as an analytical tool would require that it be periodically rezeroed in the proper ambient humidity air background.

Toluene and n-Heptane

Toluene vapor at concentrations as high as 1,300 vppm did not give a response on the XP-1. Figure 16 demonstrates that the presence of toluene vapor does not significantly alter the response profile of the corona discharge to carbon tetrachloride vapor. Figure 16 is roughly equivalent to Figure 14. Actual volumes of toluene used for these experiments were a volume equal to that of carbon tetrachloride, 10 times that of carbon tetrachloride, and 100 times that of carbon tetrachloride. These volumes represent toluene vppm concentrations of 0.25, 2.5, and 25 times that of carbon tetrachloride vppm concentrations, based on relative vapor pressures at ambient temperature. Figure 16 does show a rather pronounced error in response, as reflected in the poor precision of some of the data points. This observed lack of precision could be due to detector noise, the ambiguity of reading the LED lights, or perhaps even due to poor air flow characteristics past the sensor tip in the "T."

n-Heptane vapor at concentrations as high as 2,000 vppm did not give a response on the XP-1. Figure 17 demonstrates that the presence of n-heptane vapor does not significantly alter the response profile of the corona discharge to carbon tetrachloride vapor; Figure 17 is roughly equivalent to Figure 14. Actual volumes of n-heptane used for these experiments were a volume equal to that of carbon tetrachloride, 10 times that of carbon tetrachloride, and 100 times that of carbon tetrachloride. These volumes represent n-heptane vppm concentrations of 0.4, 4.0, and 40 times that of carbon tetrachloride vppm concentrations, based on relative vapor pressures at ambient temperature. As previously observed in the toluene environment studies, there was a relatively poor precision in the carbon tetrachloride response in the n-heptane vapor environment.

Soil Spiking

The soil spiking study was conducted using a riverbank soil obtained locally. One-gram portions of soil were weighed into individual Tedlar bags, and various concentrations of carbon tetrachloride in a 100-uL methanol aliquot were added to the soil by micropipette. The bags were immediately sealed, and the contents were shaken and allowed to equilibrate overnight. For comparison purposes, 100-uL aliquots were also spiked into empty Tedlar bags containing no soil. The results of the spiking studies are shown in Figure 18. Any variation between the soil spike data (w) and the empty bag data (w/o) is unobservable due to the lack of precision in the data, as noted above. Of particular interest is the relationship between the spiked mg VOC/Kg soil concentrations and vppm results. This correlation is influenced by the volume of the Tedlar bag (~ 1-L volume), and implies that a lower detection limit and quantitation range can be achieved by decreasing the headspace volume or increasing the amount of soil.

Sensor Interchangeability

The studies described above were conducted using one of the two original sensor tips shipped with the unit, which was labeled sensor #2 in the laboratory. Three replacement sensors (#3 through #5) were subsequently evaluated for their response to carbon tetrachloride vapor. Figure 19 shows the relative responses of the different sensors at sensitivity level 3; Figure 20 shows them at sensitivity level 4; and Figure 21 shows them at sensitivity level 5. There is a wide variation in response between the individual sensors, which is especially evident at the more sensitive level 5 setting. These variations would have to be overcome, either by quality control or by individual sensor calibration, for the XP-1 to be used as a quantitative tool.

Model H-10A Description

The TIF H-10A (Figure 22) is a corona discharge refrigerant leak detector unit with some different design features from the XP-1. It operates on 115 V and contains a small fan located in close proximity to the sensor tip, which proved to be a better design for air flow purposes than the design of the TIF XP-1. Reliable readings were obtained by inserting the probe tip directly into the Tedlar bags, without having to use the “T” fitting and sampling pump that were required for the TIF XP-1.

The H-10A uses a flashing neon light and an audible popping signal that increases in frequency as higher amounts of halogen are detected. Since the audible frequency cannot be used directly to estimate amounts or concentrations of chemical vapors, the unit was modified by CF Electronics, Laramie, Wyoming, to provide wire leads interfaced from the audible output to a multimeter that provided a readout of the frequency in Hz. In this fashion, a reliable quantitative frequency reading from about 1–300 Hz could be recorded.

The H-10A was obtained at WRI rather late in the initial study, after the humidity, toluene, n-heptane, and soil spiking experiments had all been performed for the TIF XP-1.

However, the purpose in evaluating the H-10A was not so much for its corona discharge response profiles, because these had already been suitably obtained for the TIF XP-1. Rather, the main purpose in evaluating the H-10A was for its overall design features that distinguished it from the XP-1.

Carbon Tetrachloride

Figure 23 shows the response profile for carbon tetrachloride vapor in dry air for a single sensor tip using a background blank setting of 1, 2, and 4 Hz. The 1-Hz background setting is the least sensitive, and the 4-Hz setting is the most sensitive. Higher background settings provide erratic results. As shown in Figure 23, the lower working range of the H-10A is fairly equivalent to that of the XP-1, in the vicinity of 10 to 25 vppm carbon tetrachloride. The quantitation limit is about 10 vppm. The ability of the operator to read a frequency signal from a digital meter makes this design more attractive for quantitative work than reading the number of lights in the XP-1 display. Therefore, this unit was used for subsequent experiments.

Sensor Interchangeability

The studies described above were conducted using the two original sensor tips shipped with the unit. Three replacement sensors (#3 through #5) were subsequently evaluated for their response to carbon tetrachloride vapor. Figure 24 shows the relative responses of the different sensors at the medium blank sensitivity setting of 2 Hz. There is some variation evident in response between the individual sensors.

Tetrachloroethylene

Relative sensitivities of the corona discharge system were measured with a single sensor tip for low, medium, and high sensitivity settings for low, medium, and high concentrations of both carbon tetrachloride and tetrachloroethylene (PCE). The data are presented in Table 3. The results show that the response to tetrachloroethylene is essentially identical to the response to carbon tetrachloride. Both of these VOCs contain four chlorine atoms. PCE has a double bond. Apparently, the presence of the double bond does not affect the response or the ability of the chlorine atoms to capture electrons in the corona.

Table 3. TIF H-10A Relative Response of Carbon Tetrachloride and Tetrachloroethylene

| <u>Sensitivity</u> | <u>Instrument</u> <u>Setting</u> | <u>Concentration</u> <u>CCl₄, vppm</u> | <u>Response</u> <u>Hz/vppm</u> | <u>Concentration</u> <u>PCE, vppm</u> | <u>Response</u> <u>Hz/vppm</u> | <u>Response</u> <u>PCE/CCl₄</u> |
|--------------------|-------------------------------------|--|-----------------------------------|--|-----------------------------------|---|
|--------------------|-------------------------------------|--|-----------------------------------|--|-----------------------------------|---|

| | | | | | | |
|----------|------|------|------|------|------|-------------|
| High | 4 Hz | 30.8 | 7.38 | 29.2 | 7.15 | 0.97 |
| Medium | 2 Hz | 91.0 | 3.43 | 87.7 | 4.15 | 1.21 |
| Low | 1 Hz | 297 | 1.06 | 297 | 0.94 | <u>0.89</u> |
| Average: | | | | | | 1.02 |

Elements of a New Analytical Method

As discussed above, the performance of the new devices was evaluated in the laboratory by spiking soil samples and monitoring headspace for halogenated VOCs. A draft concept of the steps required to develop new analytical methods with these devices would require a number of considerations. These include sample collection, the container from which headspace would be sampled, and the interpretation of the signal from the sensor system. Since samples would be contaminated with VOCs, consideration must be made for collecting the sample with as little handling and loss as possible. Prior to headspace screening analysis, the sample should be placed in a container that has the ability to contract as the headspace is being drawn out, to prevent dilution by outside air. This would possibly involve using 5 g of a 25-g soil sample and 250-mL to 500-mL headspace volume. Calibration of the sensor device would be with a controlled leak source such as those available from sensor manufacturers, or standardization from a known amount of a particular VOC such as carbon tetrachloride in a Tedlar bag. Possibly, the soil sample could be dried with a drying agent prior to analysis; however, the heat generated could cause the VOC contaminants to rapidly enter the headspace. Water should not be added to the soil sample. Prior results in our laboratory show that this adds an additional complexity in that complex VOC equilibria between soil and water and air would apply, and headspace results are generally lower than when evaluating the sample directly. Quantitation limits and dynamic analytical ranges could be altered by changing the soil to air ratios and possibly temperature.

CONCLUSIONS

Commercially available heated diode and corona discharge leak detectors were obtained from the manufacturers. These were modified to provide readouts that correspond to the concentration of halogenated VOCs in air. Sensor response was evaluated with carbon tetrachloride and tetrachloroethylene (perchloroethylene, PCE), which represent halogenated

VOCs with and without double bonds. The response characteristics were determined for the VOCs directly in headspace, without soil, in containers such as Tedlar bags. Quantitation limits were established at a S/N ratio of 10. Potential interferences from volatile hydrocarbons, such as toluene and heptane, were evaluated and found to be nonexistent. The effect of humidity was studied also. Humidity did not change the response profiles, and small responses due to humidity could be zeroed out. Soil spiking experiments were conducted also. These showed that the VOCs measured in the headspace with the modified leak detectors could be used to screen halogenated VOC concentrations in soil. A draft concept of the steps required to develop new analytical methods with these devices was prepared.

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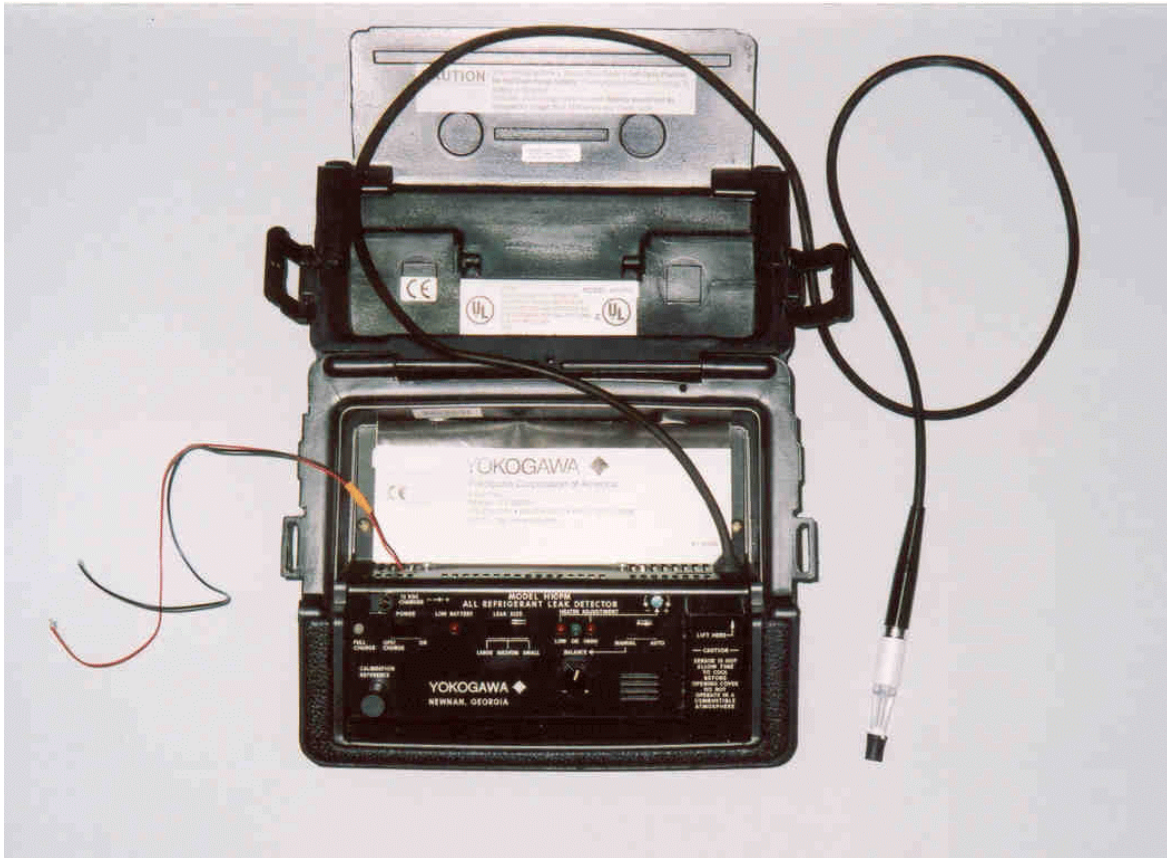


Figure 1. Yokogawa H-10PM Heated Diode Leak Detector

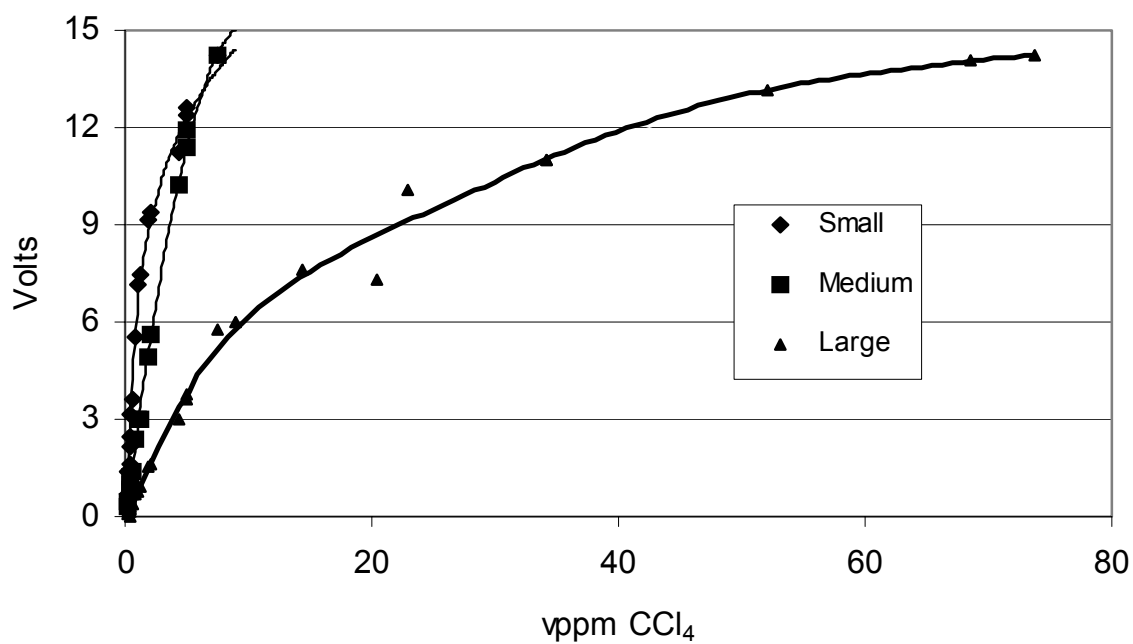


Figure 2. Response Profile of Yokogawa H-10PM

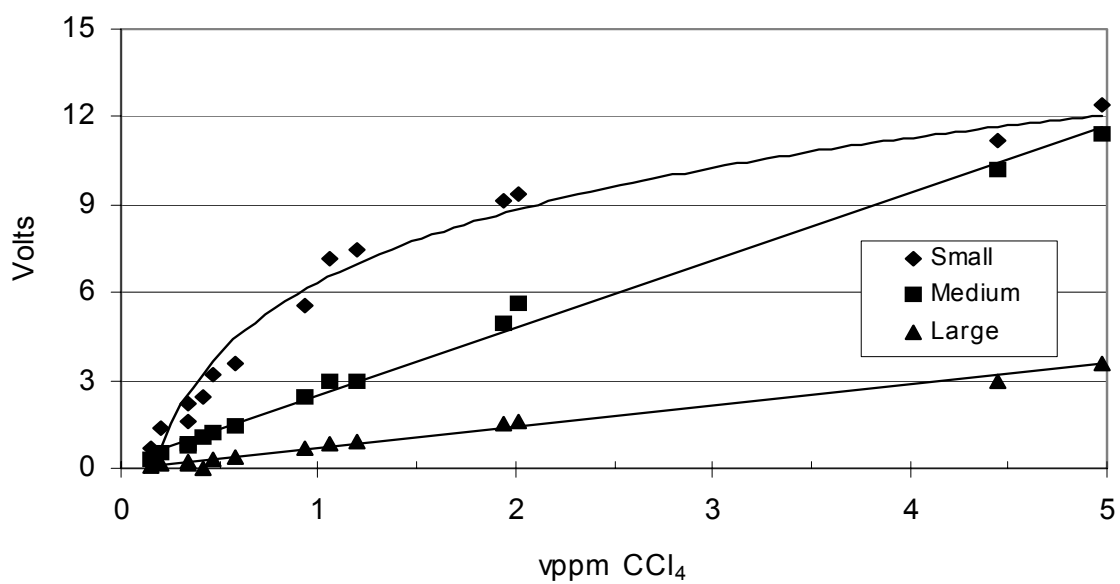
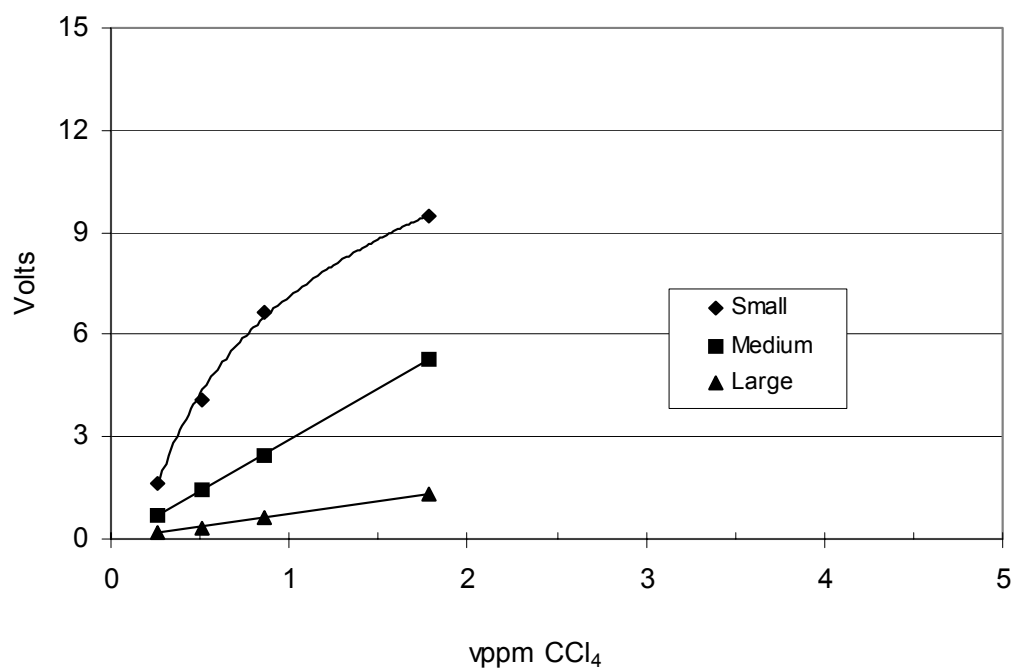


Figure 3. Expanded View of Lower Working Range of Yokogawa H-10PM



Figure

4. Yokogawa H-10PM Response Profile in Saturated Water Vapor Environment

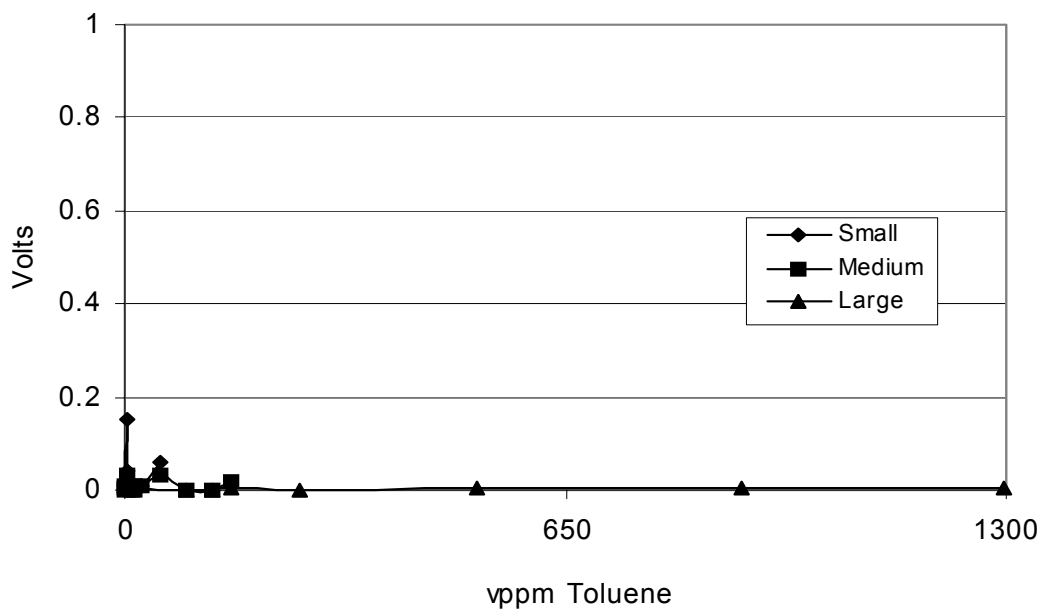


Figure 5. Yokogawa H-10PM Response to Toluene Vapor

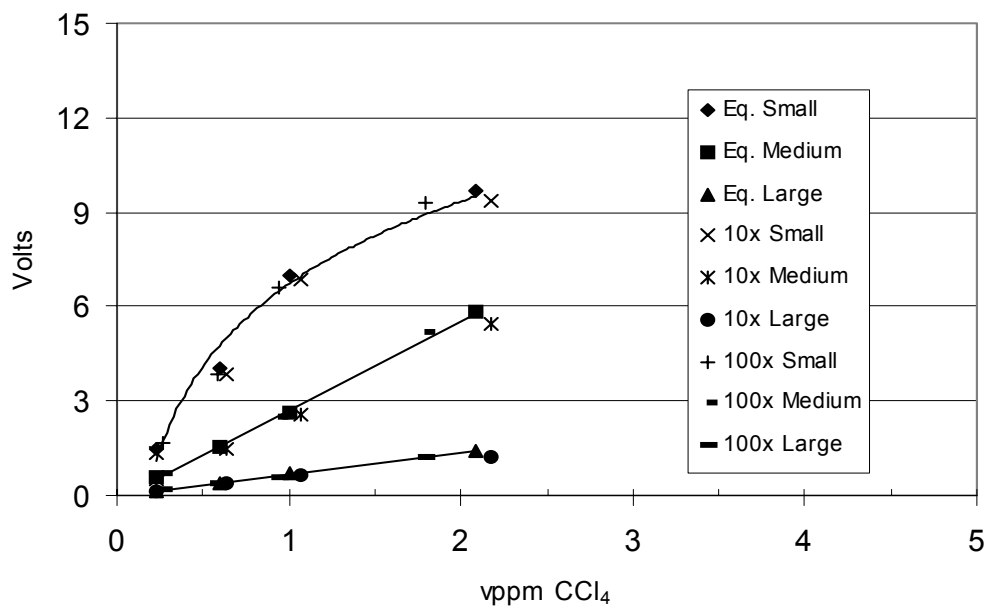


Figure 6.
Yokogawa H-10PM Response Profile in Toluene Vapor Environment

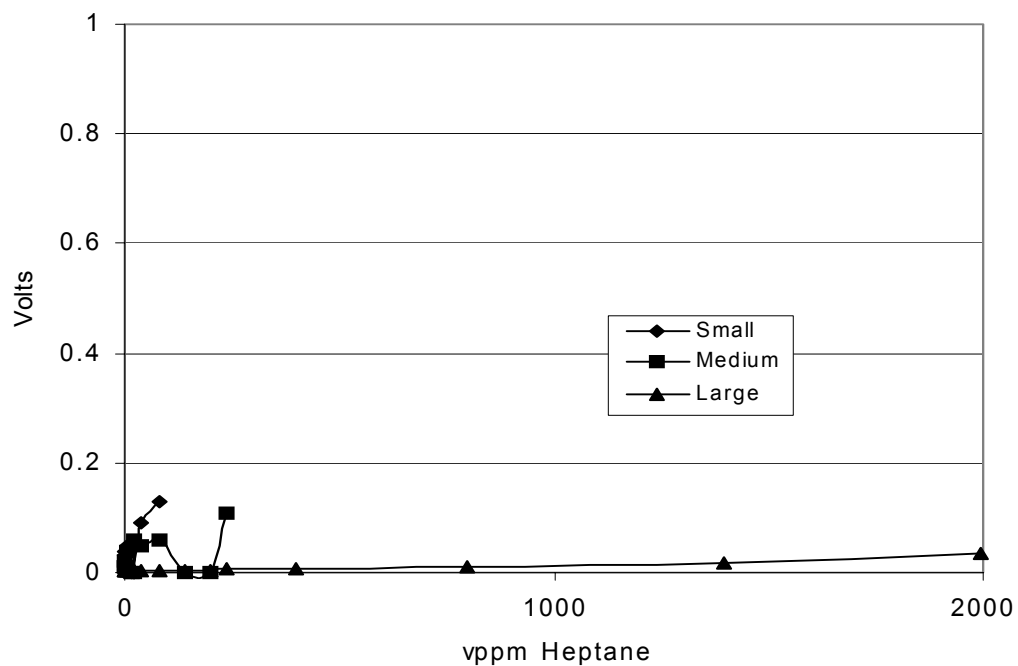


Figure 7.
Yokogawa
H-10PM Response to n-Heptane Vapor

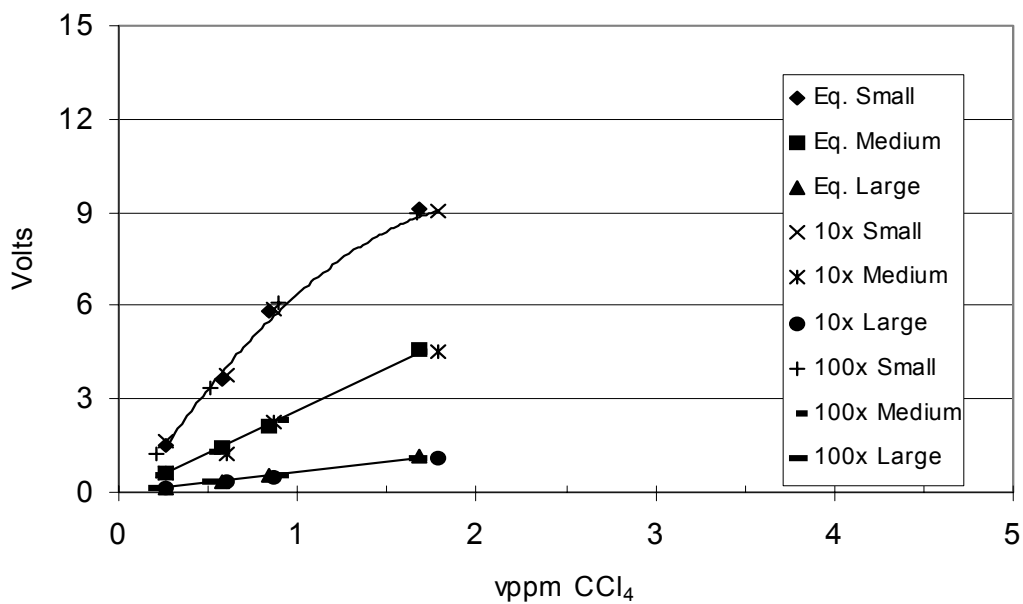


Figure 8. Yokogawa H-10PM Response in n-Heptane Vapor Environment

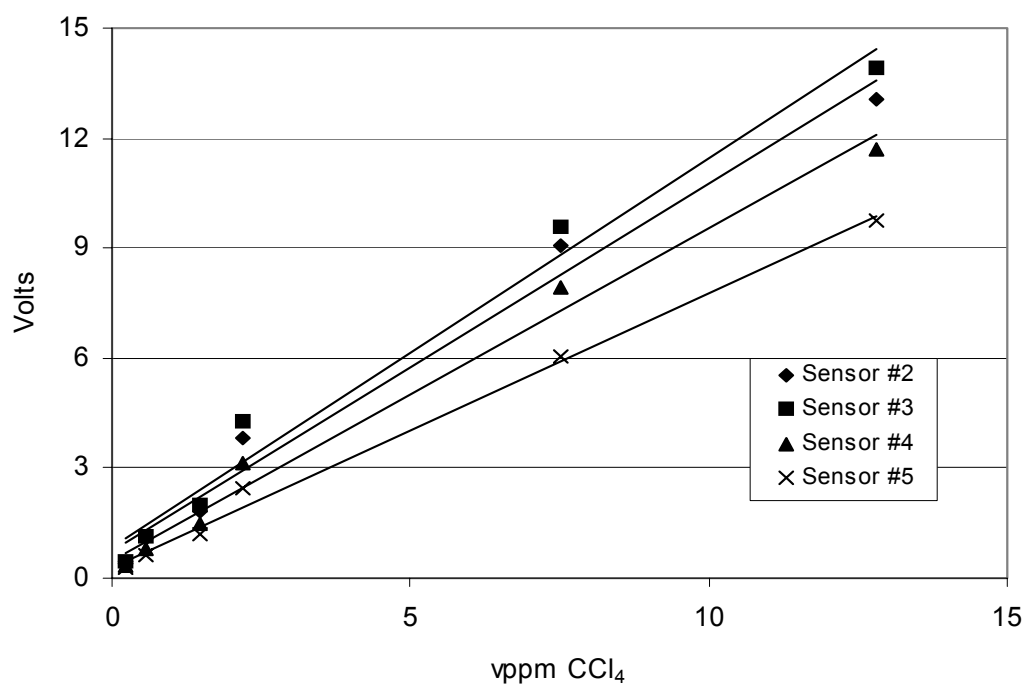


Figure 9. Yokogawa H-10PM Sensor Interchangeability

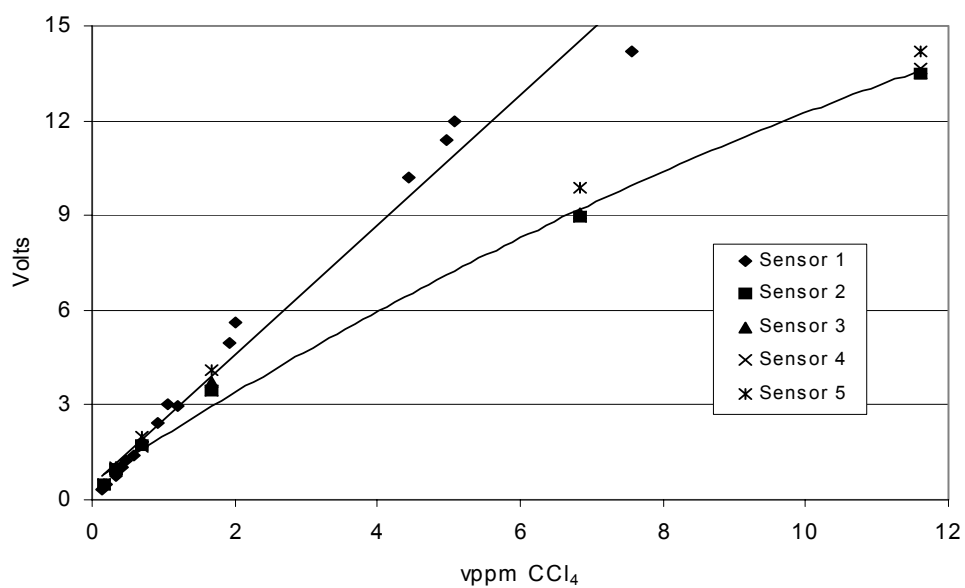


Figure 10. Yokogawa H-10PM Sensor Comparison with Temperature Adjustment

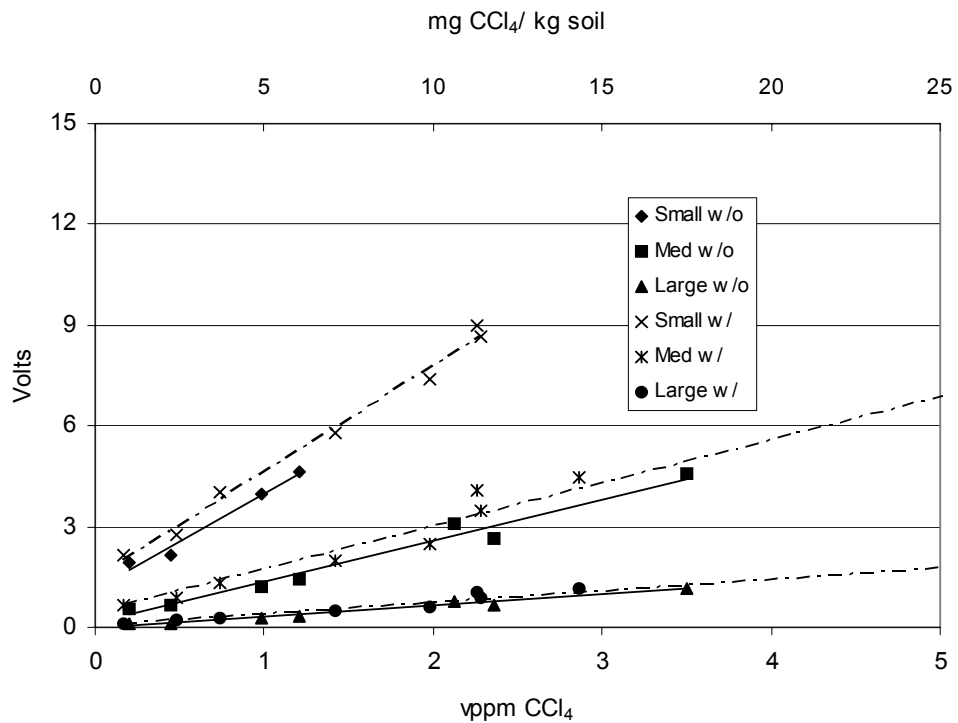


Figure 11. Yokogawa H-10PM Soil Spiking Results



Figure 12. TIF XP-1 Leak Detector with Auxiliary Du Pont P200A Personal Sampling Pump

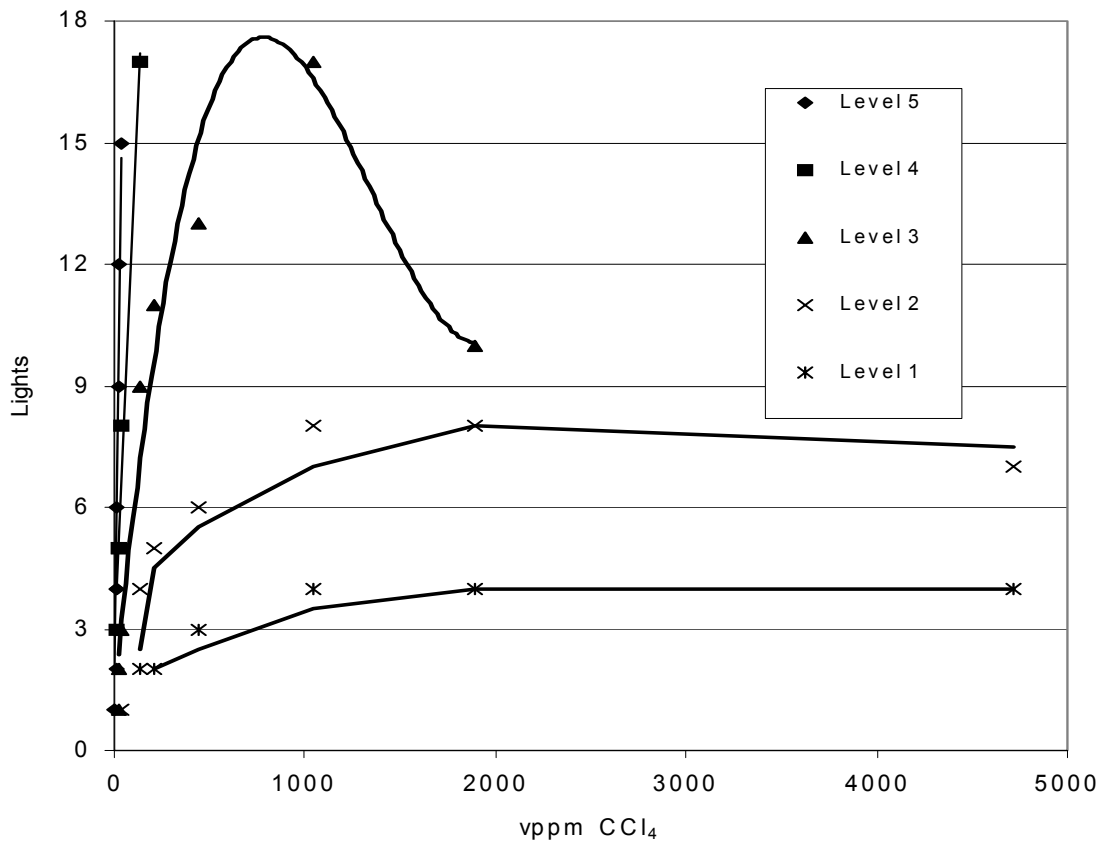


Figure 13. Response Profile of TIF XP-1

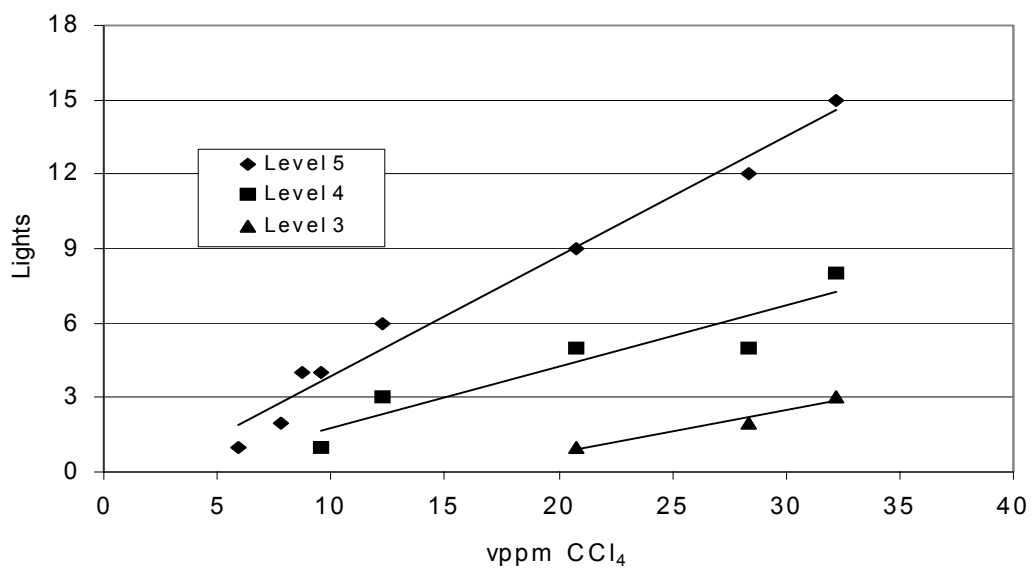


Figure 14. Expanded View of Lower Working Range of TIF XP-1

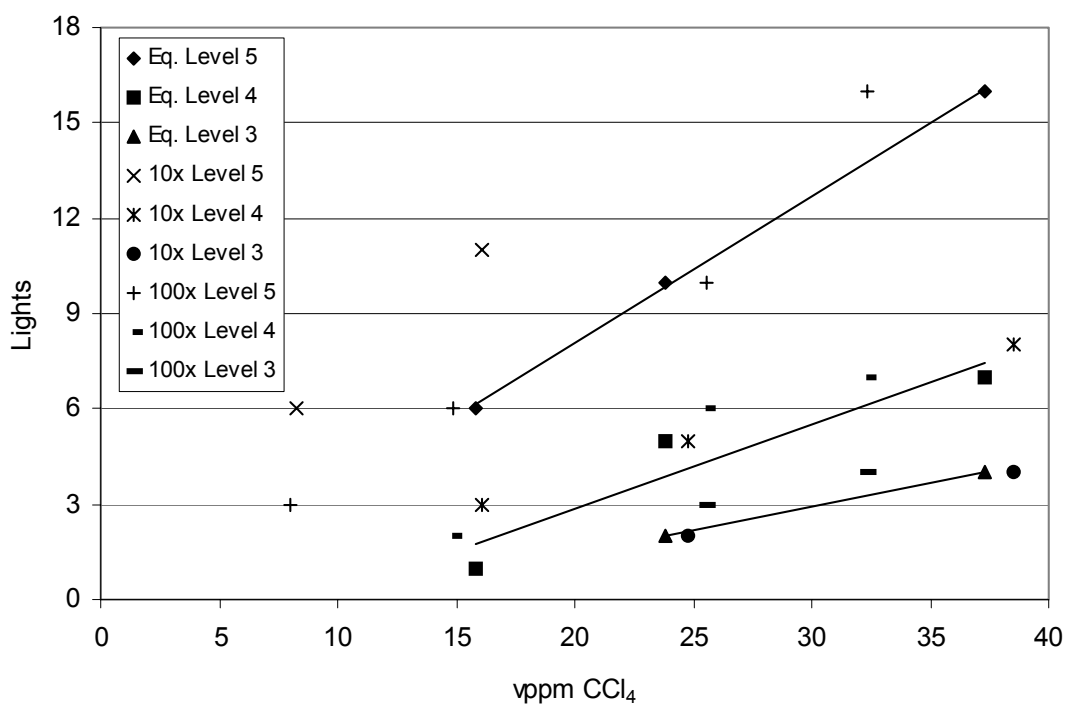
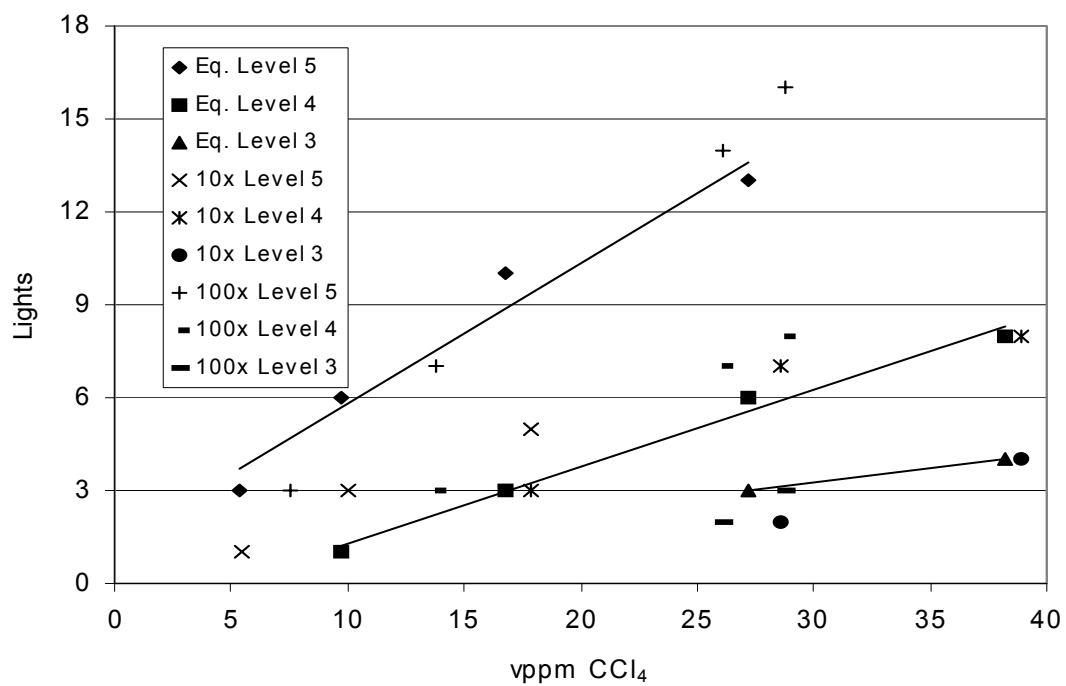


Figure 15. TIF XP-1 Response in Saturated Water Vapor Environment



e 16. TIF XP-1 Response in Toluene Vapor Environment

Figur

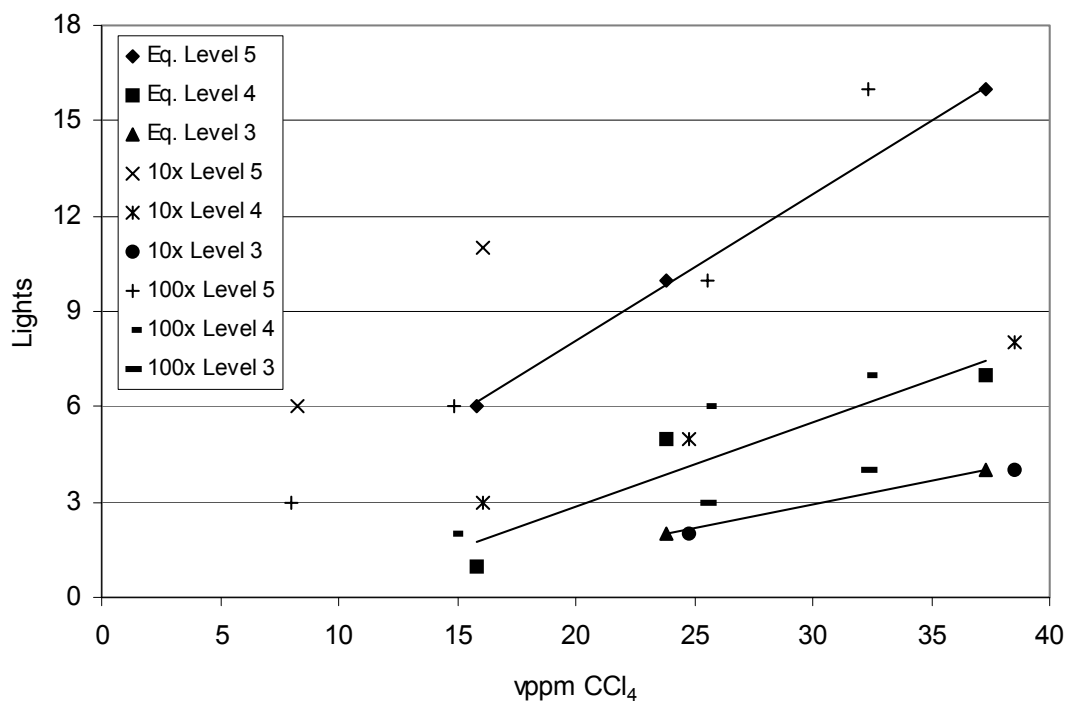


Figure 17. TIF XP-1 Response Profile in n-Heptane Vapor Environment

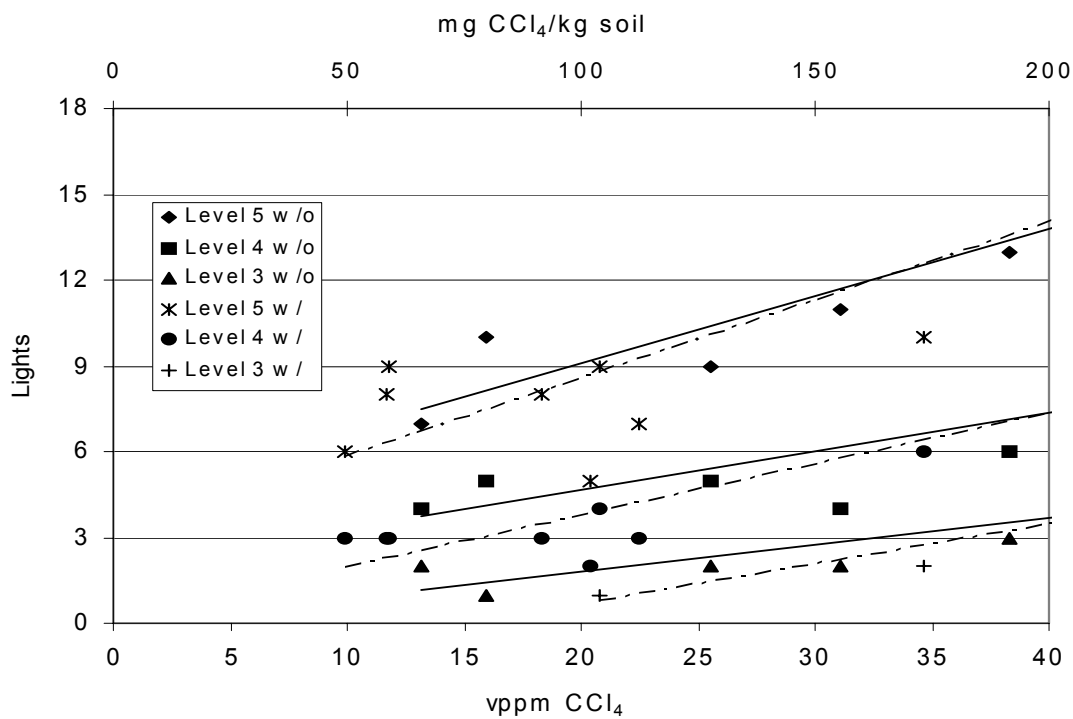


Figure 18. TIF XP-1 Soil Spiking Results

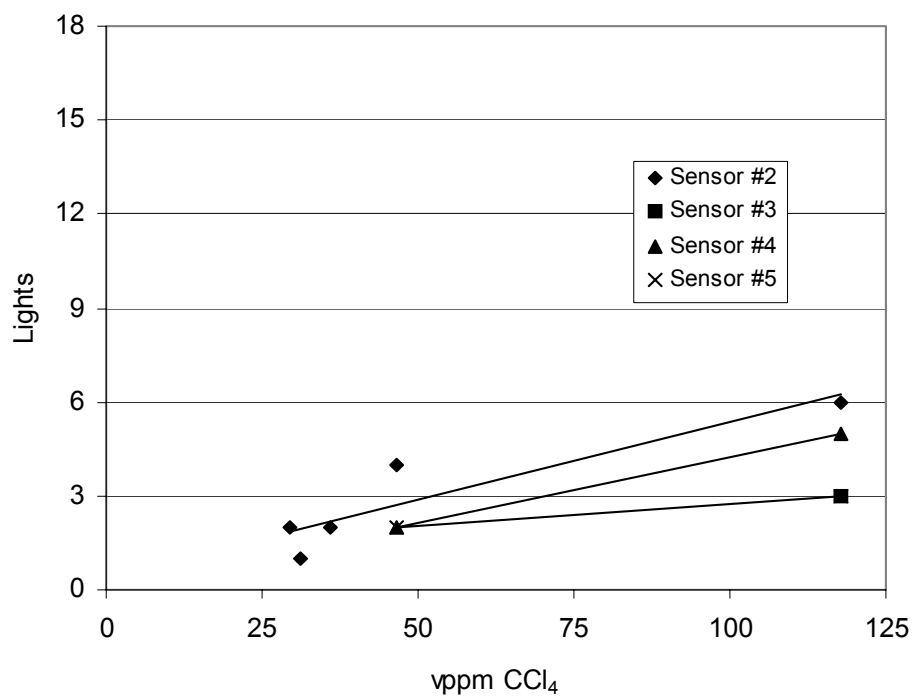


Figure 19.

TIF XP-1 Sensitivity Level 3, Sensor Interchangeability

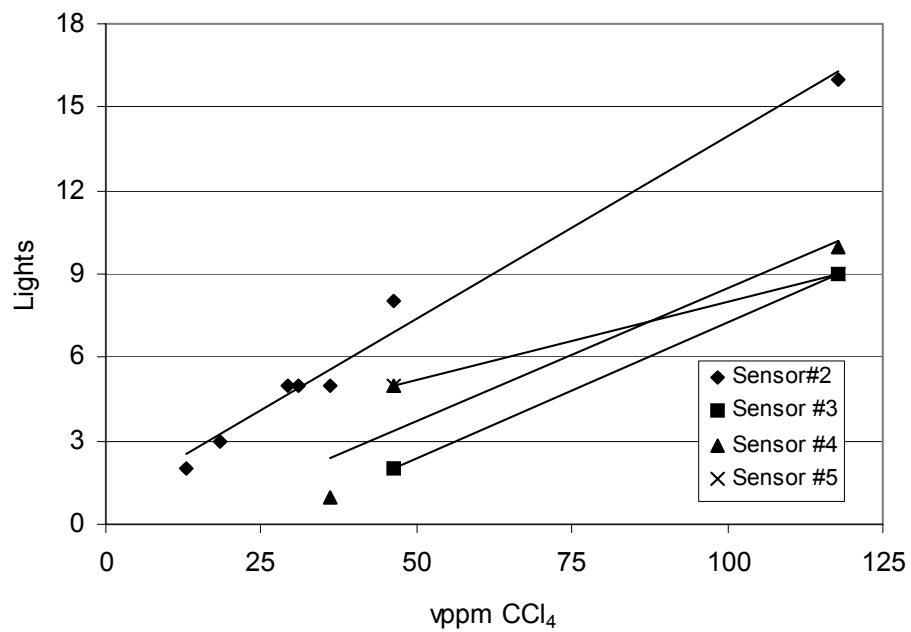


Figure 20.
TIF XP-1

Sensitivity Level 4, Sensor Interchangeability

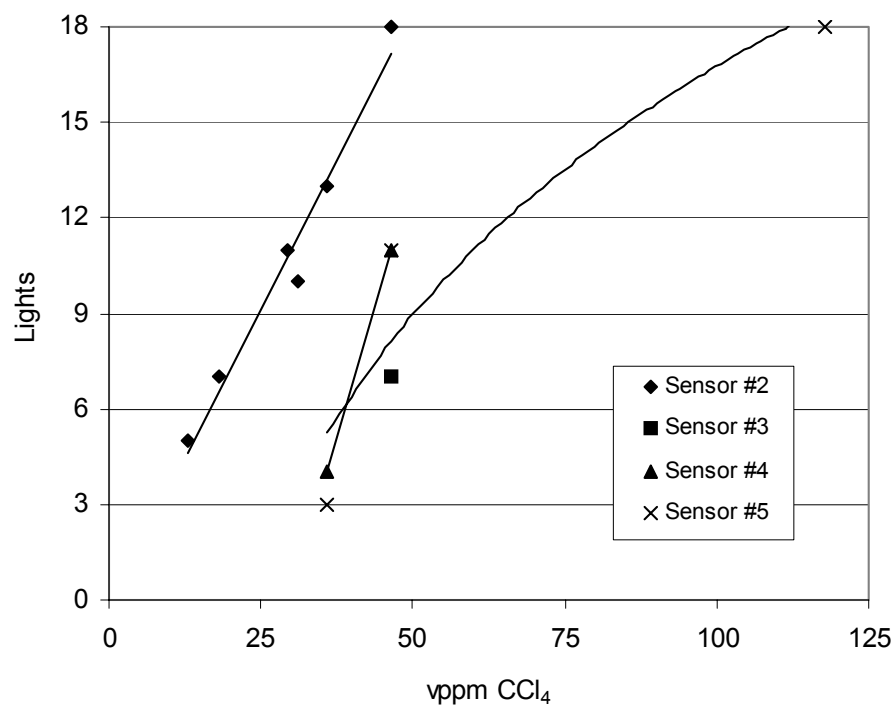


Figure 21.

TIF XP-1 Sensitivity Level 5, Sensor Interchangeability

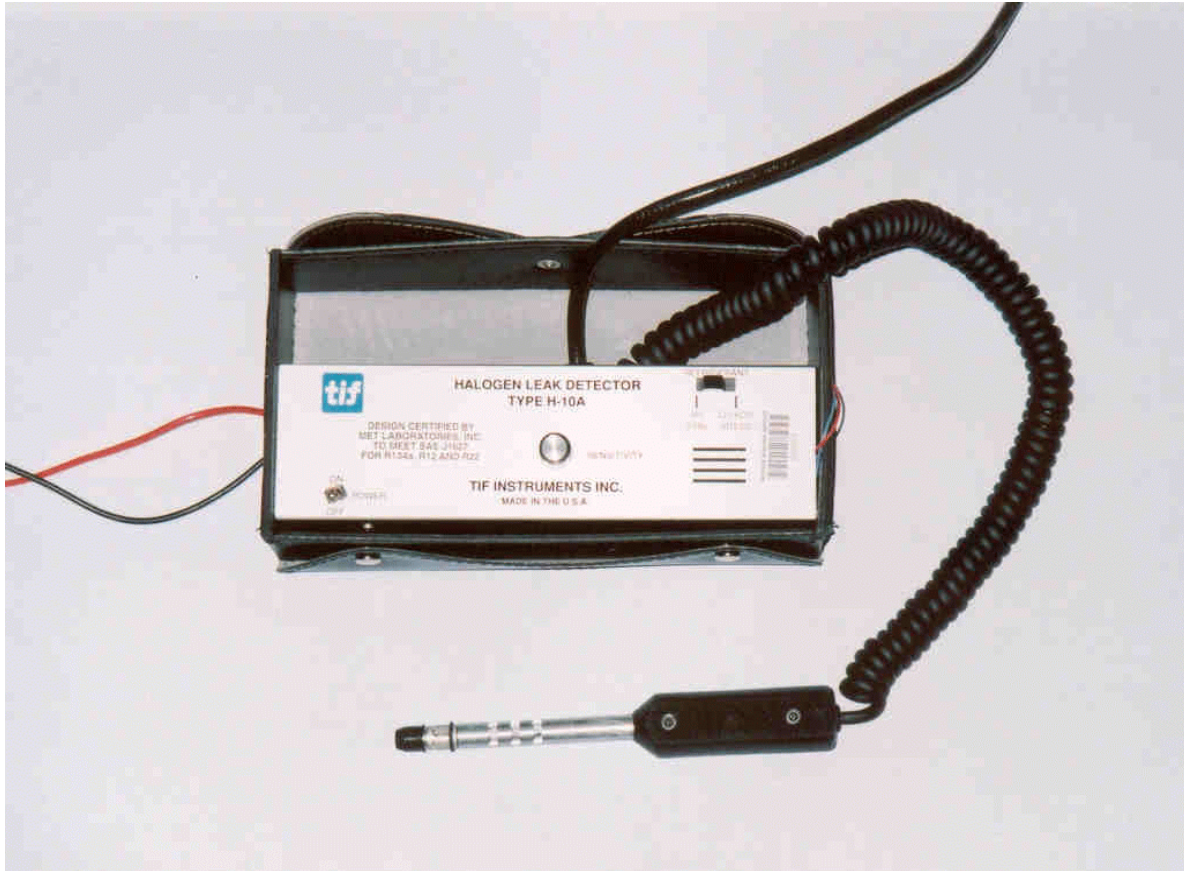


Figure 22. TIF H-10A Leak Detector

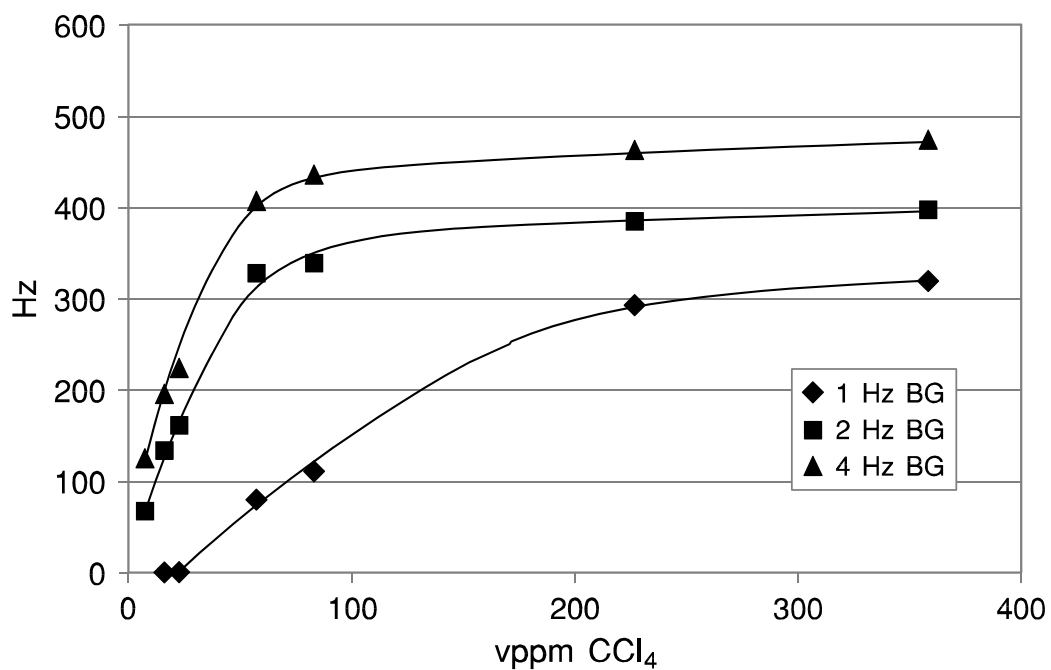


Figure 23. Response Profile of TIF H-10A

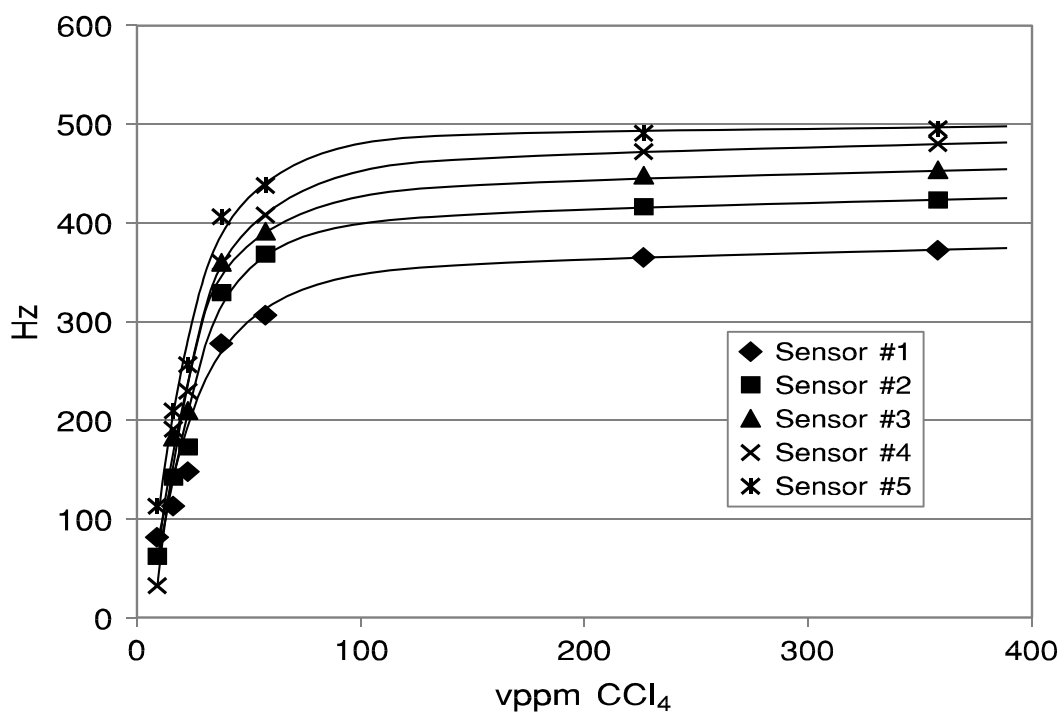


Figure 24. TIF H-10A Sensor Interchangeability