WRI-03-R006

FIELD SCREENING FOR HALOGENATED VOLATILE ORGANIC COMPOUNDS

Topical Report

By
John F. Schabron
Joseph F. Rovani, Jr.
Theresa M. Bomstad

July 2003

Work Performed Under Cooperative Agreement
DE-FC26-98FT40322 Task 3.8

For
U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory
Morgantown, West Virginia

By
Western Research Institute
Laramie, Wyoming

ACKNOWLEDGMENTS

Funding for this study was provided by the U.S. Department of Energy under Cooperative Agreement DE-FC26-98FT40322.

DISCLAIMER

ABSTRACT

Western Research Institute (WRI) is continuing work toward the development of new 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 halogens. In prior work, the devices were tested for response to carbon tetrachloride, heptane, toluene, and water vapors. In the current work, sensor response was evaluated with sixteen halogenated VOCs relative to carbon tetrachloride. The results show that the response of the various chlorinated VOCs is within an order of magnitude of the response to carbon tetrachloride for each of the sensors. Thus, for field screening a single response factor can be used. Both types of leak detectors are being further modified to provide an on-board LCD signal readout, which is related to VOC concentration. The units will be fully portable and will operate with 115-V line or battery power.

Signal background, noise level, and response data on the Bacharach heated diode detector and the TIF corona discharge detector show that when the response curves are plotted against the log of concentration, the plot is linear to the upper limit for the particular unit, with some curvature at lower levels. When response is plotted directly against concentration, the response is linear at the low end and is curved at the high end. The dynamic ranges for carbon tetrachloride of the two devices from the lower detection limit (S/N=2) to signal saturation are 4–850 vapor parts per million (vppm) for the corona discharge unit and 0.01–70 vppm for the heated diode unit. Additional circuit modifications are being made to lower the detection limit and increase the dynamic response range of the corona discharge unit.

The results indicate that both devices show potential utility for future analytical method development work toward the goal of developing a portable test kit for screening halogenated VOCs in the field.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

EXECUTIVE SUMMARY

Western Research Institute (WRI) is continuing work toward the development of new 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 halogens. In prior work, the devices were tested for response to carbon tetrachloride, heptane, toluene, and water vapors. In the current work, sensor response was evaluated with sixteen halogenated VOCs relative to carbon tetrachloride. Both types of leak detectors are being modified further to provide an on-board LCD signal readout, which is related to VOC concentration. A summary of accomplishments from the current FY 02 effort is listed below.

- Commercially available heated diode and corona discharge leak detectors were modified to provide readouts that correspond to the concentration of halogenated VOCs in air.

- Responses were evaluated in air for sixteen VOCs relative to carbon tetrachloride. The results show that the response of the various chlorinated VOCs is within an order of magnitude of the response to carbon tetrachloride for each of the sensors. Thus, for field screening a single response factor can be used.

- Two additional leak detectors of each type were procured and are being modified further to provide on-board digital readout of signal voltage, which is related to concentration. The units will be fully portable and will operate with 115-V line or battery power.

Signal background, noise level, and response data on the Bacharach heated diode detector and the TIF corona discharge detector show that when the response curves are plotted against the log of concentration, the plot is linear to the upper limit for the particular unit, with some curvature at lower levels. When response is plotted directly against concentration, the response is linear at the low end and is curved at the high end. The dynamic ranges for carbon tetrachloride of the two devices from the lower detection limit (S/N=2) to signal saturation are 4–850 vppm for the corona discharge unit and 0.01–70 vppm for the heated diode unit. For a 25-g soil sample in a 120-mL (4-oz) jar, the limits of detection for carbon tetrachloride are estimated to be 0.2 ug/kg (ppb) for the heated diode sensor and 90 ug/kg for the corona discharge sensor. The results indicate that both devices show potential utility for future analytical method development work toward the goal of developing a portable test kit for screening halogenated VOCs in the field.

OBJECTIVES

The ultimate goal of the multi-year 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 Bacharach Inc., Newnan, Georgia. Corona discharge leak monitors are commercially available from TIF (American Test Products Inc.), Mirimar, Florida. Both types of sensor systems are capable of detecting 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 CERCLA, RCRA, and municipal landfill sites. Similar observations were made 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).

The *Diesel Dog*® Soil Test Kit was developed 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 dichloromethane, require an energy of 11.7 eV for ionization (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.

Prior research at WRI has 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:

$$P_i = H_i \times C_i \tag{1}$$

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 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.

Prior Approaches to Halogenated VOC Screening

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. 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 downhole 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_2-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 toward 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 technology 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 multi-year 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 work are to obtain two widely used commercially available refrigerant leak detectors based on corona discharge and heated diode sensors, and evaluate them for possible use as field screening and monitoring devices for halogenated VOCs. 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 types of detectors are sold as alarm monitors without a digital readout.

In prior work, commercially available heated diode and corona discharge leak detectors were modified to provide readouts that correspond to the concentration of halogenated VOCs in air (Schabron et al. 2002). 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. Potential interferences from volatile fuel 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 responses due to humidity were fairly insignificant and 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.

EXPERIMENTAL DETAILS

Chemicals

The volatile halogenated VOCs were reagent grade or better from Aldrich.

Leak Detectors

The heated diode sensor was a model H-10PM refrigerant leak detector from Bacharach Inc., Newnan, Georgia. The corona discharge device was a TIF H-10A refrigerant leak detector from Advanced Test Products, Inc., Mirimar, 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 one- and five-liter 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 Bacharach 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 leak 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 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. For the detector modified with a high-impedence circuit for a readout in volts, sensitivity level adjustments were not required. A voltage readout between 0 and 6 volts was obtained using a strip chart recorder.

RESULTS AND DISCUSSION

Sensor Response

Sensor response was evaluated relative to carbon tetrachloride for sixteen commercially available VOC analytes. The VOCs varied by the number and type of halogens on the molecules. These are listed in Table 1 as six series of compounds for which the responses relative to carbon tetrachloride were determined. One compound, dichloromethane, is included in both the two halogen and the two chlorine series. The series were selected to determine the effects of numbers of chlorine atoms, the presence or absence of a double bond or aromatic ring, and the relative responses for different halogens.

Table 1. Halogenated VOC Analyte Series

Analyte Series	Analyte Name	Analyte Series	Analyte Name
Four Chlorine	Carbon Tetrachloride	*Chlorofluorocarbon*	1,1,1,2 tetrachlorodifluoroethane
	Tetrachloroethylene		1,1,2-trichlorotrifluoroethane
Three Chlorine	1,1,1-Trichloroethane	*Two-halogen methanes*	Dichloromethane
	1,1,2-Trichloroethylene		Dibromomethane
	Trichloromethane		Diiodomethane
Two Chlorine	Dichloromethane	*Halo-benzene*s	Fluorobenzene
	Trans-1,2 Dichloroethylene		Chlorobenzene
	1,1-Dichloroethylene		Bromobenzene
	1,2-Dichloroethane		Iodobenzene

Heated Diode Sensor

Model H-10PM Description

The heated diode sensor was a model H-10PM refrigerant leak detector from Bacharach Inc., Newnan, Georgia (Figure 1). This was originally manufactured by Yokogawa USA, and the technology was acquired by Bacharach in 2002. 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 VOC molecules. 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 affect the sensitivity of the device. The low flow rate provides the most sensitivity, while the highest flow rate provides the least sensitivity. To compensate for different responses when the sensor diode ages or is replaced, the diode temperature can be adjusted. A higher temperature provides greater sensitivity, but with a shortened diode service life. There is an audio alarm with a chirping sound that is indicative of the amount of volatile halogenated compounds present. Since this is a refrigerant leak detector and there is no numerical 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 (Schabron et al. 2002). Currently, WRI is modifying the device further to provide an on-board digital readout from 0.00–20.00 volts designed to capture and display the maximum voltage produced during a sample analysis.

The H-10PM has an auto zero function that provides steady readings when the unit is in this mode. Once a signal is read, the unit attempts to reset the output to zero. The initial reading is proportional to concentration. It has three sensitivity settings; small, medium, and large. The settings alter the amplified signal by changing the air flow rate to the detector, and by electronic attenuation. The small setting represents an amplified signal that provides the most sensitivity, however it becomes saturated at about 5 vppm. 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 since it reacts with the halogens it comes in contact with. 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.

Relative Response Factors

Relative sensitivities of the heated diode system were measured in dry air with a single diode at low, medium, and high sensitivity settings at low, medium, and high concentrations of carbon tetrachloride and a series of sixteen additional halogenated VOCs listed in Table 1. Responses for the various analytes were calculated as voltage per vppm concentration. The ratios of response of the analytes divided by the response of carbon tetrachloride are provided in Table 2. The average results for the three sensitivity levels are provided in Table 3. Results show that with the exception of bromobenzene and iodobenzene, all of the halogenated VOCs tested gave a response within an order of magnitude of the response of carbon tetrachloride. Tetrachloroethylene, 1,1,2-trichloroethylene, dichloromethane, dibromomethane, diiodomethane, and the halo-benzenes gave responses significantly lower than carbon tertachloride. The chlorofluorocarbons gave relative responses of 0.93 and 1.3, similar to carbon tetrachloride. The two-halo methanes all gave responses less than carbon tetrachloride in the order chloro>bromo>iodo substituents. For the halo-benzene series, flourobenzene and chlorobenzene gave responses about ten times less than carbon tertachloride, and bromobenzene and iodobenzene gave very little response. Neither of these VOCs are common analytes in environmental analyses.

Table 2. Heated Diode H-10PM Relative Response of Carbon Tetrachloride and Halogenated VOC Analyte Series

Series	Analyte	Instrument Sensitivity	Concentration, vppm CCl_4	Concentration, vppm Analyte	Response Ratio Analyte/CCl_4
Four Chlorine	Tetrachloroethylene	High	3.5	2.0	0.089
		Medium	14.4	11.2	0.21
		Low	32.5	29.8	0.25
Three Chlorine	1,1,1-Trichloroethane	High	2.7	3.3	1.1
		Medium	8.1	6.4	1.9
		Low	36.4	47.3	1.1
	1,1,2-Trichloroethylene	High	2.7	2.3	0.21
		Medium	8.1	8.1	0.55
		Low	21.0	23.3	0.33
	Trichloromethane	High	4.5	5.6	1.3
		Medium	12.7	12.9	1.7
		Low	26.4	23.3	2.4
Two Chlorine	Dichloromethane	High	2.5	3.2	0.40
		Medium	13.6	10.7	0.47
		Low	42.0	35.4	0.74
	trans-1,2-Dichloroethylene	High	3.9	3.9	1.2
		Medium	13.5	11.9	1.6
		Low	29.4	25.7	1.2
	1,1-Dichloroethylene	High	3.9	3.0	1.6
		Medium	13.5	7.7	2.1
		Low	29.4	29.5	1.3
	1,2-Dichloroethane	High	3.0	1.9	1.4
		Medium	11.7	10.5	1.1
		Low	34.0	23.6	1.0

Table 2. Heated Diode H-10PM Relative Response of Carbon Tetrachloride and Halogenated VOC Analyte Series (continued)

Series	Analyte	Instrument Sensitivity	Concentration, vppm CCl_4	Analyte	Response Ratio Analyte/CCl_4
CFC	1,1,1,2-Tetrachlorodifluoroethane	High	5.8	2.4	0.94
		Medium	8.3	6.4	0.94
		Low	31.3	25.2	0.91
	1,1,2-Trichlorotrifluoroethane	High	3.3	4.9	1.3
		Medium	11.1	15.5	1.3
		Low	31.6	27.7	1.3
Two-halogen methanes	Dichloromethane	High	2.5	3.2	0.40
		Medium	13.6	10.7	0.47
		Low	42.0	35.4	0.74
	Dibromomethane	High	4.8	1.7	0.22
		Medium	6.7	8.5	0.49
		Low	30.2	24.3	0.50
	Diiodomethane	High	4.8	1.7	0.04
		Medium	6.7	6.5	0.18
		Low	30.2	29.8	0.12
Halo-benzene	Fluorobenzene	High	3.9	2.6	0.32
		Medium	13.4	8.0	0.38
		Low	30.9	33.0	0.18
	Chlorobenzene	High	3.9	4.5	0.12
		Medium	13.4	9.6	0.20
		Low	30.9	29.7	0.14
	Bromobenzene	High	3.6	2.8	0.09
		Medium	13.0	7.2	0.06
		Low	35.3	29.5	0.04
	Iodobenzene	High	2.7	2.6	0.01
		Medium	12.1	10.8	0.00
		Low	33.0	30.0	0.00

Table 3. Heated Diode H-10PM and Corona Discharge H-10A Average Relative Response to Carbon Tetrachloride (Analyte/CCl_4) for Halogenated VOC Analyte Series

Series	Analyte	Heated Diode H-10PM	Corona Discharge H-10A
Four Chlorine	Tetrachloroethylene	0.18	1.0
Three Chlorine	1,1,1-Trichloroethane	1.4	0.92
	1,1,2-Trichloroethylene	0.36	0.80
	Trichloromethane	1.8	1.2
Two Chlorine	Dichloromethane	0.54	0.17
	trans-1,2 Dichloroethylene	1.3	1.1
	1,1-Dichloroethylene	1.7	1.2
	1,2-Dichloroethane	1.2	0.34
CFC	1,1,1,2-Tetrachlorodifluoroethane	0.93	1.4
	1,1,2-Trichlorotrifluoroethane	1.3	1.6
Two-halogen methanes	Dichloromethane	0.54	0.17
	Dibromomethane	0.40	1.1
	Diiodomethane	0.11	0.08
Halo-benzene	Fluorobenzene	0.11	0.00
	Chlorobenzene	0.15	0.49
	Bromobenzene	0.06	0.28
	Iodobenzene	0.004	1.2

Detection Limit for Carbon Tetrachloride

Figure 2 shows the response profile of the Bacharach H-10PM to carbon tetrachloride vapor in dry air with the unit set at the large leak setting, which is the least sensitive but provides the largest dynamic range. This profile was obtained at ambient room temperature at an elevation of 7,200 feet. Corrections have not been made for other temperatures or elevations. The profile for the large setting provides a curved response up to about 70 vppm, where the response has maximized to a saturated signal output near 15 V. When response is plotted directly against concentration, the response is linear at the low end and is curved at the high end. Signal background and noise level and response data show that when the response curves are plotted against the log of concentration, the plot is linear to the upper limit of 70 vppm, with some curvature at lower levels (Figure 2).

Noise at the large setting was estimated to be about 3 mV. The dynamic range for carbon tetrachloride from the lower detection limit (S/N=2) to signal saturation is 0.01–70 vppm for the heated diode unit. For a 25-g soil sample in a 4-ounce jar, assuming a headspace of 120 cc, the detection limit of about 0.01 vppm in air corresponds to about 0.2 ug/kg in soil. The upper end of the dynamic range possibly can be increased by providing a larger flow rate past the diode, lowering the temperature on the diode, or adding a mechanical splitter to dilute the sample vapors with air as they enter the detector.

Corona Discharge Sensor

Model H-10A Description

The TIF H-10A (Figure 3) is a corona discharge refrigerant leak detector unit that operates on 115 V and contains a small fan located in close proximity to the sensor tip to provide air movement across the tip. There are two sensitivity settings. The hydrochlorofluorocarbon (HCFC) setting is the most sensitive and it was used in the current study. The less sensitive setting is chlorofluorocarbons (CFC). Readings were obtained by inserting the probe tip directly into the Tedlar bags containing sample vapors in air.

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 (Schabron et al. 2002). Three sensitivity levels were obtained by setting the background sensitivity to 1, 2, or 4 Hz to obtain a quantitative frequency reading from about 1–300 Hz. The 4-Hz setting is the most sensitive, and the 1-Hz setting is the least sensitive.

Later in the study, the unit was modified further by CF Electronics using a high-impedence voltage readout circuit to obtain a direct reading proportional to the voltage on the corona tip. Although the voltage signal is somewhat noisy, it is possible to capture the maximum voltage during a sample analysis using a strip chart recorder. The best sensitivity and maximum dynamic range were obtained when the frequency sensitivity was set at 0 mHz, and there was no audible or frequency response during the reading. The advantage of using the voltage readout is that the operator does not need to adjust the sensitivity of the unit. All readings from low to high concentrations are obtained at a single setting.

The H-10A is currently being modified further for operation on a 12-v gel acid battery and to enclose it in a new case to include the battery, charger, and 0.01 to10.00-volt LCD digital readout with maximum signal capture capability (Figure 5). Circuit modifications are being made to decrease the noise to provide a lower detection limit, and to increase the upper dynamic range.

Relative Response Factors

Relative sensitivities of the corona discharge system were measured before the voltage readout modification with a single sensor tip for low, medium, and high sensitivity baseline settings for low, medium, and high concentrations of carbon tetrachloride and the various series of halogenated VOCs listed in Table 1. Responses for the various analytes were calculated as frequency (Hz) per vppm concentration. The ratios of response of the analytes divided by the response of carbon tetrachloride are provided in Table 4. The average results for the three sensitivity levels are provided in Table 3. Results show that with the exception of diiodomethane and fluorobenzene, all of the halogenated VOCs tested gave a response within an order of magnitude of the response of carbon tetrachloride. Dichloromethane, 1,2-dichloroethane, chlorobenzene, and bromobenzene gave responses significantly lower than carbon tertachloride. The chlorofluorocarbons gave relative responses of 1.4 and 1.6. For the two-halogen series, dibromomethane responded similar to carbon tetrachloride, and dichloromethane and diiodomethane provided significantly lower responses. For the halo-benzene series, flourobenzene gave no response. This VOC is not a common analyte in environmental analyses. Iodobenzene gave a response slightly greater than carbon tetrachloride. Chlorobenzene and bromobenzene had relative responses of 0.49 and 0.28, respectively.

Detection Limit for Carbon Tetrachloride

As mentioned, the H-10A unit was modified with a high-impedence circuit that allowed for a direct voltage readout using a strip chart recorder. The response profile for carbon tetrachloride using the voltage readout is provided in Figure 4. This profile was obtained at ambient room temperature at an elevation of 7,200 feet. Corrections have not been made for other temperatures or elevations. When response is plotted directly against concentration, the response is linear at the

Table 4. Corona Discharge H-10A Relative Response of Carbon Tetrachloride and Halogenated VOC Analyte Series

Series	Analyte	Instrument Sensitivity	Concentration, vppm CCl_4	Analyte	Response Ratio Analyte/CCl_4
Four Chlorine	Tetrachloroethylene	High	30.8	29.2	1.0
		Medium	91.0	87.0	1.2
		Low	297	280	0.9
Three Chlorine	1,1,1-Trichloroethane	High	36.4	47.3	0.93
		Medium	89.2	112	0.87
		Low	285	311	0.96
	1,1,2-Trichloroethylene	High	20.9	23.3	0.70
		Medium	89.2	114	0.78
		Low	255	274	0.92
	Trichloromethane	High	26.4	23.3	1.7
		Medium	102	132	0.86
		Low	288	307	1.0
Two Chlorine	Dichloromethane	High	42.0	35.4	0.42
		Medium	128	101	0.10
		Low	226	286	0.00
	trans-1,2-Dichloroethylene	High	29.4	25.7	1.3
		Medium	104	122	0.89
		Low	317	334	1.0
	1,1-Dichloroethylene	High	29.4	29.5	1.0
		Medium	104	86.4	1.2
		Low	317	264	1.3
	1,2-Dichloroethane	High	34.0	23.6	0.54
		Medium	105	93	0.47
		Low	448	257	0.00

Table 4. Corona Discharge H-10A Relative Response of Carbon Tetrachloride and Halogenated VOC Analyte Series (continued)

		Instrument	Concentration, vppm		Response Ratio
Series	Analyte	Sensitivity	CCl_4	Analyte	Analyte/CCl_4
CFC	1,1,1,2-Tetrachlorodifluoroethane	High	31.3	25.2	1.6
		Medium	111	93.3	1.4
		Low	390	348	1.2
	1,1,2-Trichlorotrifluoroethane	High	31.6	27.7	1.8
		Medium	155	86.1	2.0
		Low	302	320	1.0
Two-halogen methanes	Dichloromethane	High	42.0	35.4	0.42
		Medium	128	101	0.10
		Low	226	286	0.00
	Dibromomethane	High	30.2	24.3	1.0
		Medium	127	89.2	1.4
		Low	365	290	1.1
	Diiodomethane	High	30.2	29.8	0.24
		Medium	127	134	0.00
		Low	365	386	0.00
Halo-benzene	Fluorobenzene	High	30.9	33.0	0.00
		Medium	128	112	0.00
		Low	294	360	0.00
	Chlorobenzene	High	30.9	29.7	0.59
		Medium	128	128	0.65
		Low	294	281	0.22
	Bromobenzene	High	35.3	29.5	0.33
		Medium	116	136	0.52
		Low	343	383	0.00
	Iodobenzene	High	33.0	30.1	1.3
		Medium	90.0	77.9	1.3
		Low	301	312	1.0

low end and is curved at the high end (Figure 4). Signal background and noise level and response data for the TIF H-10A corona discharge detector show that when the response curves are plotted against the log of concentration, the plot is linear to the upper limit of about 850 vppm, with some curvature at lower levels. At higher concentrations there is some nonlinearity due to the amplifier circuit. Signal noise was estimated to be about 0.08 V. Circuit modifications are being made to reduce this noise and lower the detection limit.

The dynamic ranges for carbon tetrachloride from the lower detection limit (S/N=2) to signal saturation are 4–850 vppm for the corona discharge unit. For a 25-g soil sample in a 4-ounce jar, assuming a headspace of 120 cc, the detection limit of 4 vppm in air corresponds to a detection limit of about 90 ug/kg (ppb) soil. The detection limit can possibly be lowered by modifying the electronic circuit to decrease the noise. The working dynamic range possibly can be increased by improving the amplifier circuit. Preliminary experiments show that the corona discharge unit has not yet reached saturation at a carbon tetrachloride concentration of about 20,000 vppm. The upper dynamic range can possibly be increased by providing a larger flow rate past the corona tip or adding a mechanical splitter to dilute the sample vapors.

Alcohol Interference

Volatile alcohols can cause a response from both the corona discharge and heated diode detectors. Selectivity ratios for methanol, ethanol, and isporopanol were calculated based on detector response from alcohol vapors when portions of the alcohols were injected into Tedlar bags and allowed to evaporate (Table 5). The selectivity ratios are the equivalent concentration of alcohol required to provide a detector response equivalent to 1 vppm carbon tetrachloride. The heated diode detector at the low sensitivity setting had selectivity ratios for the alcohols ranging from 1,200 to 76,000 at concentration levels ranging from 620 to 76,000 vppm. The corona discharge detector at the 1-Hz baseline sensitivity setting showed no response for alcohol concentrations ranging from 4,100 to 7,600 vppm. At alcohol concentrations about ten times greater than this, the selectivity ratios ranged from 430–320,000. The results indicate that screening analyses for the presence of halogenated VOCs should not be conducted in the presence of significant levels of alcohol vapors, such as alcohol extracts or alcohol-contaminated soils. For comparison, the IDLH (immediate danger to life and health) levels for methanol, ethanol, and ispropanol are 6,000, 1,000, and 2,000 vppm, respectively.

The X-Wand^{TM} Detector

Both the heated diode and corona discharge detectors are being modified and put into new packaging designed for field screening for halogenated VOCs in the field. These modifications are currently under way. A name proposed for this new product line is the X-Wand^{TM} Halogen OVA. Figure 5 shows an early modification of a corona discharge unit with an X-Wand OVA cover plate. These units will be evaluated for response to carbon tetrachloride, dynamic range, and potential interferences as part of the ongoing effort.

Table 5. Heated Diode H-10PM and Corona Discharge H-10A Selectivity Ratios of Alcohols to Carbon Tetrachloride

		Selectivity Ratio	
Alcohol	vppm	Heated Diode (Low Setting)	Corona Discharge (1-Hz Setting)
Methanol	1,100	11,000	nd
	7,600	76,000	nd
	76,000	59,000	320,000
Ethanol			
	800	2,700	nd
	5,300	8,800	nd
	53,000	1,400	430
Isopropanol	620	1,200	nd
	4,100	4,100	nd
	41,000	7,500	1,500

A New Analytical Method

A draft concept of the steps required to develop new analytical methods with these devices requires a number of considerations. These include sample collection to maintain the integrity of the sample prior to analysis, the container from which headspace is 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. Various techniques for soil VOC sample collection are described in ASTM D 4547, Standard Guide for Sampling Waste and Soils for Volatile Organic Compounds (ASTM 2002). For downhole soil sampling, the new AccuCore^{TM} sampler could be used in conjunction with the Geoprobe penetrometer to eliminate subsampling on the surface, which results in significant VOC loss. Prior to headspace screening analysis, the sample should be placed in a container that has the ability to contain the headspace once a soil core sample is placed in it. It should allow for sampling by the detector device with minimal dilution by outside air. This would possibly involve using a 5-g or 25-g soil sample and a 120-mL to 500-mL headspace volume jar or bag. Calibration checks 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 or isopropyl alcohol in a Tedlar bag or jar. Possibly, the soil sample could be dried with a drying agent prior to analysis; however, any heat generated by the drying agent reacting with water could cause the VOC contaminants to rapidly enter the headspace. Water should not be added to the soil sample, since it can suppress the passage of volatile analytes from the soil to the air headspace. Prior results in WRI's 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. Signal interpretation could be simplified by defining the concentration in terms of order of magnitude. For example, in terms of carbon tetrachloride, the signal readout could correspond to not detected, low (up to 10 vppm), medium (10–100 vppm), and high (>100 vppm) ranges. Conversion to soil vppm would be derived from a calculation using the vppm range in the headspace, the soil weight, and the volume of headspace. Quantitation limits and dynamic analytical ranges could be altered by changing the soil to air ratios and possibly the temperature.

EPA SW-846 Method 5035, Closed-System Purge-And-Trap And Extraction For Volatile Organics In Soil And Waste Samples, defines low-level (<200 : g/kg) and high-level (>200 : g/kg) sample preparation methods for VOCs in soil (USEPA 1996). Method 5035 is a sample preparation method that must be used with an analysis method such as Method 8260B, Volatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS). Method 8260B lists the estimated quantitation limit (EQL) for most VOCs at 5 : g/kg, the lowest concentration that can be reliably achieved. The EQL is generally 5–10 times the detection limit. Typical detection limits for VOCs in soils using GC/MS are on the order of 0.5–1.0 : g/kg.

CONCLUSIONS

Commercially available heated diode and corona discharge leak detectors were modified to provide numerical readouts that correspond to the concentration of halogenated VOCs in air. Sensor responses with sixteen VOCs relative to the response of carbon tetrachloride were obtained. The responses for the chlorinated VOCs are within an order of magnitude of the response for carbon tetrachloride. This suggests that for field screening, a single response factor can be used. Signal background, noise, and response data on the heated diode detector and the corona discharge detector show that when the response curves are plotted against the log of concentration, the plots are linear to the upper limit for the particular unit, with some curvature at lower levels. When response is plotted directly against concentration, the responses are linear at the low end and are curved at the high end. The dynamic ranges for carbon tetrachloride from the lower detection limit (S/N=2) to signal saturation are 0.01–70 vppm for the heated diode unit and 4–850 vppm or higher for the corona discharge unit. This corresponds to detection limits for a 25-g soil sample with 120-mL headspace of about 0.2 ug/kg for the heated diode unit and 90 ug/kg for the corona discharge unit. The upper dynamic range limits of the detectors can be increased by modifying the air flow across the detectors or providing a mechanical splitter to dilute the sample with air. Detection limits can be improved by using more soil and less headspace. The results show that the modified leak detectors can be used to screen halogenated VOC concentrations in soil with detection limits comparable to the EPA GC/MS laboratory methods.

REFERENCES

Adams, J.W., W.M. Davis, E.R. Cespedes, W.J. Buttner, ans M.W. Findlay, 1997, Development of Cone Penetrometer Electrochemical Sensor Probes for Chlorinated Solvents and Explosives, Field Analytical Methods for Hazardous Wastes and Toxic Chemicals, Conference Proceedings, Air & Waste Management Association, Pittsburgh, PA, 667-670.

American Society for Testing and Materials, 2000, D-5831-96, Standard Test Method for Screening Fuels in Soils. *Annual Book of ASTM Standards*, Vol. 11.04, 319-326.

American Society for Testing and Materials, 2002, D4547-98, Standard Guide for Sampling Waste and Soils for Volatile Organic Compounds. *Annual Book of ASTM Standards*, Vol. 11.04, 31-40.

Buttner, W.J., W.R. Penrose, J.R. Stetter, C.E. Christy, and C. Naklaishi, 1995, A Hand-Portable Instrument System for Real-Time Analysis of Chlorinated Organic Compound Contamination, Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Conference Proceedings, Volume 2, Air & Waste Management Association, Pittsburgh, PA, 702-712.

Driscoll, J.N. and J.H. Becker, 1979, Industrial Hygiene Monitoring with a Variable Selectivity Photoionization Detector, American Laboratory, 11 (11): 101-110.

Ewing, K.J., T. Bilodeau, G. Nau, F. Bucholtz, and I.D. Aggarwal, 1995, Fiber Optic Raman Volatile Organic Compound Sensor, Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Vol. 1, Conference Proceedings, Air & Waste Management Association, Pittsburgh, PA, 364-371.

Frye, G.C., D.W. Gilbert, C. Colburn, R.W. Cernosek, and T.D. Steinfort, 1995, Above-Ground In-Situ Field Screening of VOCs Using a Portable Acoustic Wave Sensor (PAWS), Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Volume 2, Conference Proceedings, Air & Waste Management Association, Pittsburgh, PA, 715-726.

Haas, J.W., M.M. Carraba, and R.W. Forney, 1995, Nonaqueous Phase Liquids: Searching for the Needle in the Haystack, Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Vol. 1, Conference Proceedings, Air & Waste Management Association, Pittsburgh, PA, 443-449.

Hewitt, A.D. and N.J. Lukash, 1997, Rapid Method for Estimating the Total Concentration of Volatile Organic Compounds in Soil Samples, Field Analytical Methods for Hazardous

Wastes and Toxic Chemicals, Conference Proceedings, Air & Waste Management Association, Pittsburgh, PA.

Hudak, R., J. Melby, D. Onisk, and J. Stave, 1995, Validation of an Immunoassay Field Screen for Trichloroethylene (TCE), Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Vol. 1, Conference Proceedings, Air & Waste Management Association, Pittsburgh, PA 101-108.

Kerndorff, H., R.H. Plumb, R. Schleyer, and G. Milde, 1992, Anthropogeochemistry of Ground-Water 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.

Le Goullon, D. and K. Goswami, 1990, Fiber Optic Refractive Index Sensor Using a Metal Clad. U.S. Patent 4,929,049.

Linenberg, A., 1995, On-Site Monitoring of Vinyl Chloride at Part Per Trillion Levels in Air, Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Vol. 1, Conference Proceedings, Air & Waste Management Association, Pittsburgh, PA, 236-245.

Milanovich, F.P., S.B. Brown, B.W. Colstron, Jr., P.F. Daley, and K.C. Langry, 1994, A Fiber-Optic Sensor System for Monitoring Chlorinated Hydrocarbon Pollutants, Talanta, 41 (12), 2189-2194.

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.

Myers, K.F., J.M. Brannon, R.A. Karn, C.B. Price, D.Y. Eng, A.B. Strong, and S.S. Cooper, 1995, Laboratory Evaluation of a Volatile Organic Compound Analysis System for the Site Characterization and Analysis Demonstration System, Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Vol. 1, Conference Proceedings, Air & Waste Management Association, Pittsburgh, PA, 177-184.

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.

REFERENCES (continued)

Oxenford, J.L., S.M. Klainer, T.M. Salinas, L. Todechiney, 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.

Schabron, J.F., J.F. Rovani, Jr., and T.M. Bomstad, 2002, Field Screening for Halogenated Volatile Organic Compounds, WRI Report 02-R013 to DOE under Cooperative Agreement DE-FC26-98FT40322.

Schabron, J.F. and J.F. Rovani, Jr., 1997, Practical Deviations from Henry's Law for Water/Air Partitioning of Volatile Organic Compounds, Proceedings of the 1997 USEPA/A&WMA International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Air & Waste Management Association, 417-426.

Schabron, J.F., J.F. Rovani, Jr., and D.F. Moore, 1996, Down Hole Photoionization Detection of Volatile Organic Compounds, WRI Report 96-R003 to DOE under Cooperative Agreement DE-FC21-93MC30127.

Schabron, J.F., N.D. Niss, B.K. Hart, and S.S. Sorini, 1995, Remote Chemical Sensor Development: A New Field Screening Method for Soil Fuel Contamination. Laramie, WY, WRI Report WRI-95-R016.

Schabron, J.F., N.D. Niss, and B.K. Hart, 1991, Application and State of Development for Remote Chemical Sensors in Environmental Monitoring, a Literature Review, DOE Report DOE/MC/11076-3063.

Sorini, S.S. and J.F. Schabron, 1997, Development and Precision Testing of a Standard Test Method for Screening Fuels in Soils. *Journal of Testing and Evaluation*, *JTEVA*, Vol. 25, No. 4, pp. 400-405.

Stach, J., J. Flachowsky, M. Brodacki, and H.R. Doring, 1995, Field Screening for Volatile Organochlorine Compounds Using Ion Mobility Spectrometry, Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Vol. 2, Conference Proceedings, Air & Waste Management Association, Pittsburgh, PA, 1046-1050.

REFERENCES (continued)

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.

U.S. Department of Energy Office of Industrial Technologies Report, 1998, "Petroleum Industry of the Future, Energy and Environmental Profile of the U.S. Petroleum Refining Industry," prepared by Energetics, Inc., Columbia, MD.

U.S. Environmental Protection Agency, 1996, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW846), Third Edition, U.S. Government Printing Office, Washington, D.C.

Walt, D.R, 1998, Fiber Optic Imaging Sensors, Accounts of Chemical Research, 31, 267-278.

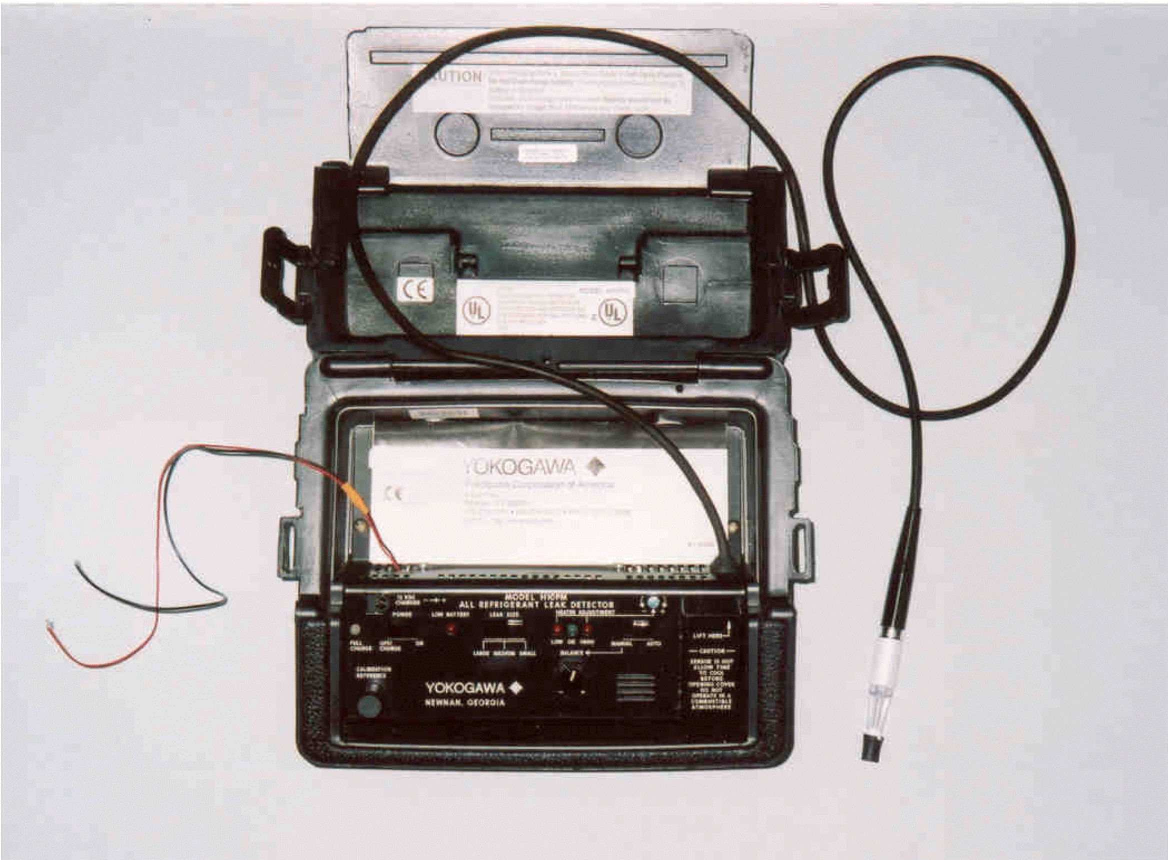

Figure 1. Bacharach H-10PM Heated Diode Leak Detector

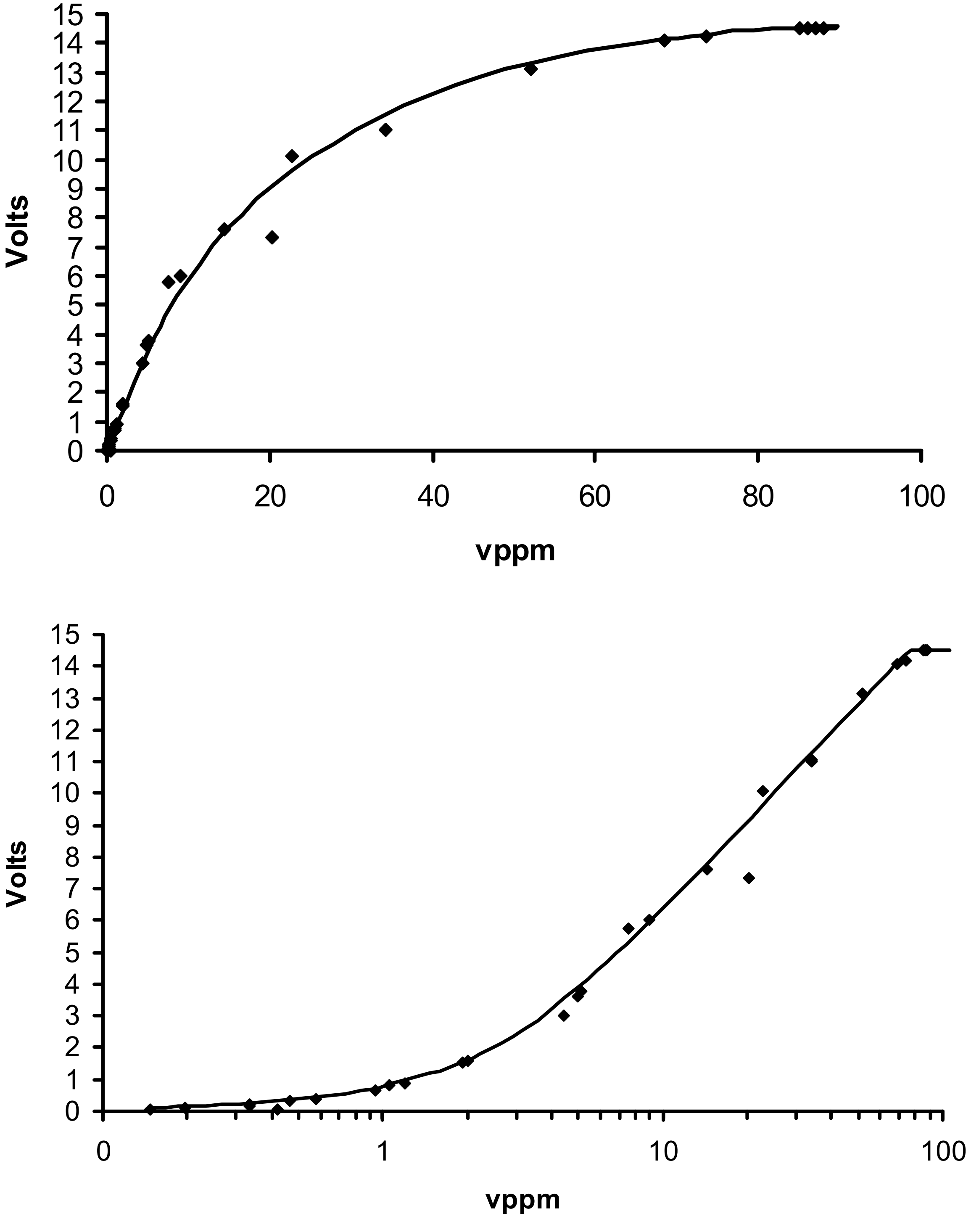

Figure 2. Response for Carbon Tetrachloride with Modified Bacharach H-10PM Detector

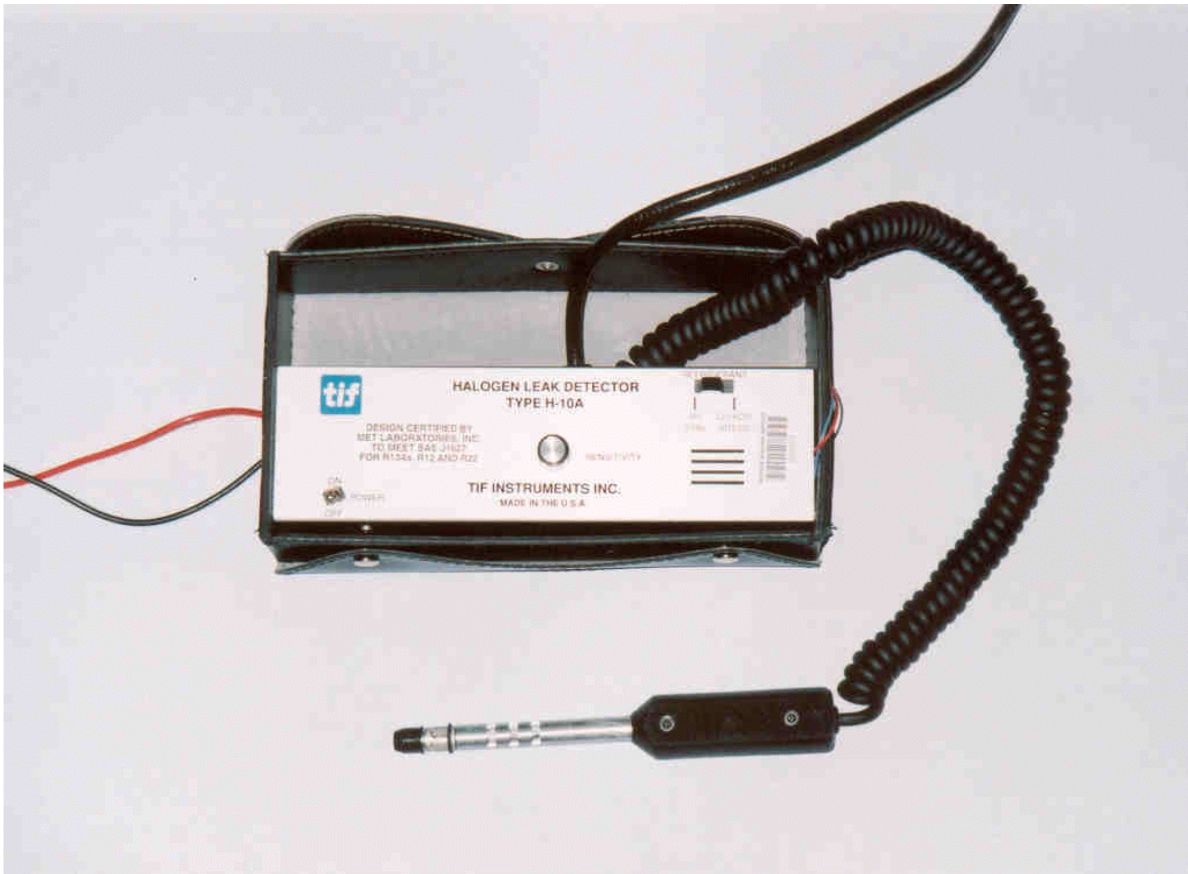

Figure 3. TIF H-10A Corona Discharge Leak Detector

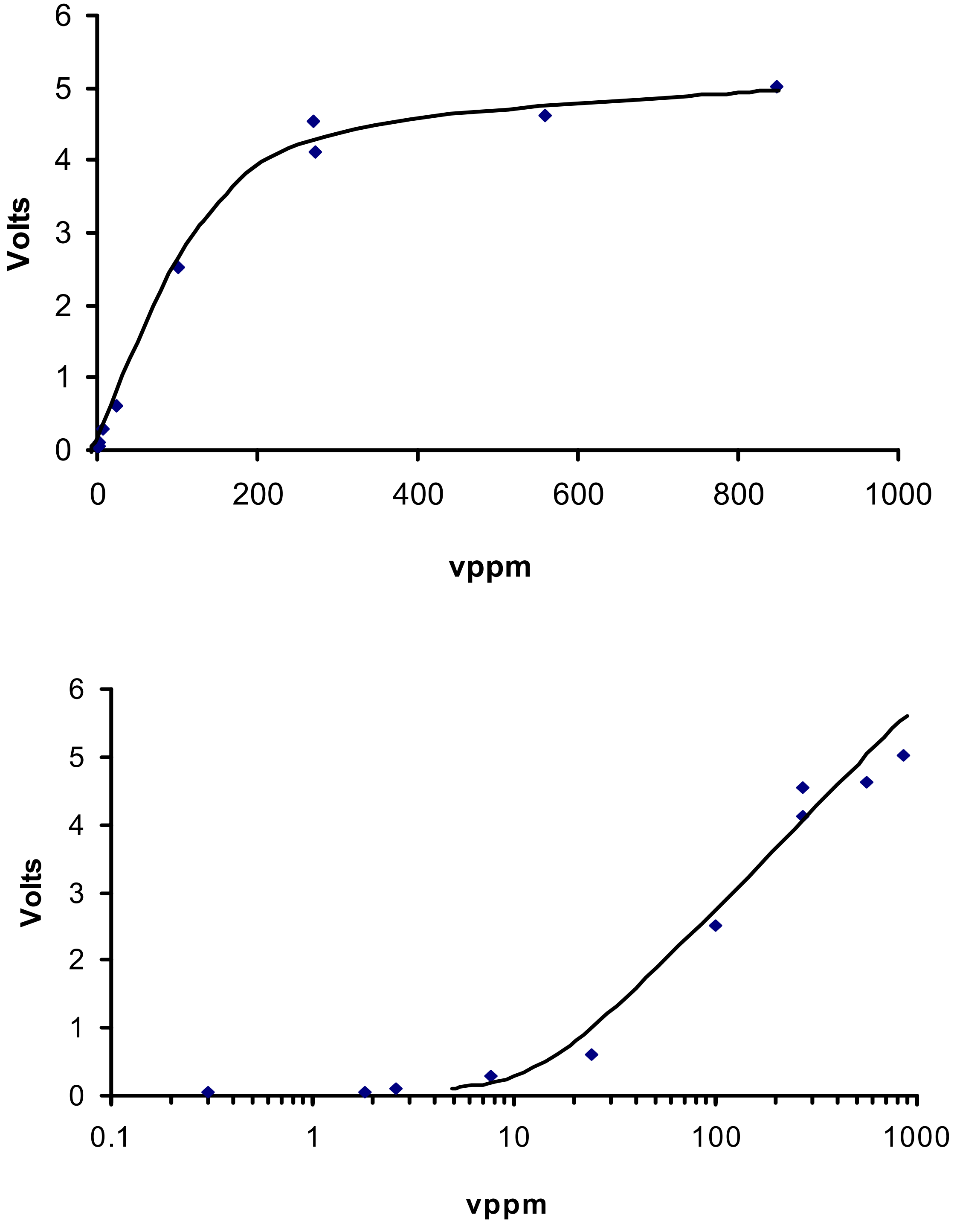

Figure 4. Response for Carbon Tetrachloride with Modified TIF H-10A Detector

Figure 5. X-Wand Corona Discharge OVA Prototype