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Adapting the Brüel and Kjær Multi-gas Monitor Type 1302 to Measure Selected Volatile Organic Chemicals (VOCs) in Soil*

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ABSTRACT

The Brüel and Kjær Multi-gas Monitor Type 1302 can simultaneously measure up to five different volatile organic chemicals (VOCs) in a single air sample by using optical filters combined with a photo acoustic detection method. The monitor has previously been validated to measure VOCs in water, by purging aqueous samples into Tedlar™ bags. The method used to measure VOCs in water has been adapted for use with soil. Soil samples are diluted with water and VOCs are purged with air from the resulting slurry into a Tedlar™ bag. The contents of the Tedlar™ bag are then analyzed with the multi-gas monitor. Data have been generated for the measurement of chloroform, trichloroethylene, tetrachloroethylene, carbon tetrachloride, and acetone. The method is linear for these VOCs from approximately 1 to at least 128 µg/g of soil (ppm). There is no measurable cross interference of these VOCs with each other when more than one is present in a single soil sample. Contaminants other than those being measured may interfere with detection of these VOCs, so some prior site characterization is required. The method is easy to perform, rapid, reproducible, and sensitive enough for field screening applications.

INTRODUCTION

Volatile organic compounds are among the most commonly found contaminants at waste sites in the Department of Energy (DOE) complex[1]. Real time, fieldable instruments that are sensitive and specific for these contaminants could help streamline assessment and restoration at these sites. One objective of the Field Methods program at Oak Ridge National Laboratory (ORNL) is to define commercially available screening methods for contaminants of interest to DOE. Our approach involves:

- Selection of potentially useful methods
- Modification or adaptation of methods, if necessary
- Experimental evaluation of methods
- Transfer of validated methods to appropriate users

Experimental evaluation of methods considers analyte specificity, limits of detection, precision, accuracy, linearity, and the working range of the method, as well as cost and time per analysis. Transfer of validated methods to appropriate users includes submission of method protocols to the *DOE Methods for Evaluating Environmental and Waste Management Samples*[2].

The Brüel and Kjær Multi-gas Monitor Type 1302 has been evaluated under this program for use in the analysis of volatile organic compounds (VOCs) in soil. This instrument was developed to monitor up to five different VOCs at a time in a single air sample. The detection method is based on a photo acoustic detector using different optical filters to specify the individual compounds to be measured. The monitor can compensate measurements for temperature fluctuations, water vapor interference, and cross interference from other compounds being measured. Over 20 optical filters are available and have been used by the manufacturer to measure over 200 different organic compounds in air samples. In this evaluation, the multi-gas monitor was validated to measure and cross compensate for chloroform, trichloroethylene (TCE), tetrachloroethylene (PCE), carbon tetrachloride, and acetone in soil samples. Acetone was included in this analysis because it is a common component of contaminated soil samples. In order for the monitor to compensate for possible interference of acetone with other VOCs, it has to be measured concurrently. The method that was previously validated for purging VOCs from water[3] was adapted to efficiently purge them from soil samples.

EXPERIMENTAL METHODS

Equipment and Materials

Brüel and Kjær Multi-gas Monitor Type 1302. The Brüel and Kjær Multi-gas Monitor Type 1302 is a microprocessor controlled air monitor. Vapor measurement with the multi-gas monitor is based on the capacity of molecules to absorb energy in the form of infrared light and release energy in the form of heat. An air sample is drawn into the instrument and sealed in a sample analysis cell. Pulses of infrared light pass through an optical filter and into the cell. Light only passes through one optical filter at a time so only a single wavelength of light is transmitted into the analysis cell at any given time. The transmitted light is selectively absorbed by the gas being monitored, and the temperature of that gas increases. As the light is pulsating, the temperature of the gas increases and decreases, causing an equivalent increase and decrease in the pressure inside the closed cell, or an acoustic signal. This acoustic signal is directly proportional to the concentration of the gas present in the cell. Two microphones are mounted inside the cell to measure the signal. When the measurement for one compound has been made, the carousel holding the filters turns. The infrared light is directed through the next optical filter, which is a wavelength tailored to a different compound, and the new signal is measured[4]. It takes approximately two minutes to measure five compounds and water vapor in one sample.

The monitor is factory or user calibrated so that it compensates measurement of each compound for interference from the other compounds being measured and from water vapor. Results of each measurement, either in ppm or in mg/m^3, are shown immediately on the front panel LCD display, and may also be sent to a printer for a running log. The most recent set of measurements is stored in the monitor's short term memory, and may be transferred to long term memory for later retrieval. Data may be transferred from short or long term memory to a printer, or to an ASCII text file and then imported into spreadsheet format for analysis. Software is available from Brüel and Kjær to perform the latter translation.

Purge Apparatus. Any purge module that is adaptable to standard 40 mL volatile organic analysis (VOA) vials is suitable. Compressed air and nitrogen are suitable purge gasses; air was used in this evaluation. Other equipment and materials necessary to purge soil samples include:

- a heavy duty magnetic stirrer (such as a Cole Parmer "9 x 9"; heating is not necessary)
- Star Head™ Nalgene magnetic stirring disks, ½" height x $^{9}/_{16}$" diameter (Nalge Co., available from VWR Scientific)
- 40 mL capacity VOA vials with Teflon lined caps or septa (depending on the purge module)
- 1 liter capacity Tedlar™ bags
- 13 mm Swinny stainless steel filter holder containing a 10 µm Teflon filter
- 25 mm, 10 µm Teflon filters
- Tygon tubing, ¼" OD x ⅛" ID
- Teflon tubing
- Flow meter to adjust the purge rate
- Deionized water
- 25 mL capacity graduated cylinder

Procedure

Summary. The method incorporates two steps in sample preparation and analysis. In the first step, VOCs are purged from the soil sample into a Tedlar™ bag. In the second step, the gas sample in the Tedlar™ bag is sampled and analyzed by the multi-gas monitor. Problems concerning loss of volatile compounds from soil samples can be associated with sample handling and transportation. For field use, therefore, the first step in which VOCs are purged from the sample should be performed as close as possible in space and time to actual sample collection. The purged samples can be analyzed with the multi-gas monitor at the sampling site, or transferred to another on-site location for analysis.

Purge. The purge flow was set at 100 ±2 mL/minute. A magnetic stirring disk was placed into a 40 mL vial and a 5 g soil sample was added. An aliquot (0.1 - 12.8 mL) of a VOC standard (25 or 50 ppm) in deionized water was added to the vial, and the total volume in the vial was brought to approximately 25 mL with deionized water. For the mixtures of VOCs used to determine cross interference, aliquots of four different VOC standards were added to one vial before the final dilution. The vial was attached to the purge module and set on a heavy duty magnetic stirrer. The outlet of the purge module was connected with a short piece of Tygon tubing through a filter inside the Swinny filter holder to the open/close valve of a one liter Tedlar™ bag. (Note: All other connecting tubing was Teflon.) This filtering step was a precaution to ensure that soil and water were not blown over into the bag. The stirrer was turned on, and the sample was purged for 10 minutes into the Tedlar™ bag. These purge conditions were dictated by the volume used by the multi-gas monitor for one measurement (approximately 280 mL), and the decision at ORNL to obtain three measurements per soil sample. Under the temperature conditions in this study, 22 - 24°C, greater than 95% of each of the analytes (except acetone) was purged with one liter of air. Significant differences in temperature may affect the completeness of sample purging, so it is important to determine purge rates under actual conditions of sample analysis, if possible.

Multi-gas Monitor Set Up. Optical filters were installed in the monitor and calibrations were made at the manufacturer prior to this evaluation. The working parameters of the multi-gas monitor set at ORNL are organized in an "inverted tree." The "Set-Up" button on the front panel of the instrument is at the top of the tree. There are three branches to choose from: configuration, measurement, and format. Parameters are entered by following the branches and entering data or selecting responses. Under the configuration branch, units are set up for concentration, length, temperature, and atmospheric pressure. For this evaluation, results were reported in mg/m^3 and converted to µg/g of soil. Also under the configuration branch, communication parameters are set if data is to be sent to a printer, and the current date and time are entered. Under the measurement branch, the monitor is set to sample continuously, so that it will draw a sample approximately every two minutes. It is also set to measure the desired analytes (designated A - E) and water vapor, and to compensate for water vapor and cross interference. The length of the sampling tube, and the actual atmospheric pressure and temperature are also set under the measurement branch. The sampling tube length was set to 0 meters for this evaluation in order to minimize the volume of gas taken for each measurement. Under the format branch, the instrument was set to print each gas for this evaluation, because a running log of each measurement was kept.

Sample Measurement. After a spiked soil sample was purged into a Tedlar™ bag, the bag was attached to the inlet of the multi-gas monitor. A section of Teflon tubing (⅛" ID, approximately 40 cm) should be attached to the inlet for this purpose, and fitted to a 10 µm filter when no bag is attached. A total of three samples were withdrawn from each bag at a rate of approximately one sample every two minutes. The Tedlar™ bag must be removed from the inlet after sampling is complete, or a vacuum will be created and an error message will result. Results for the five analytes and water vapor are shown on the front panel of the monitor at the end of a measurement, and printed out simultaneously on the attached printer. This running printout is not necessary, however; data is stored in the instrument's short term memory and may be printed out later or transferred to a computer. At the end of each day's analyses, a summary of all of the measurement results and system parameters was made. If a printer is not available, the data may be saved in the monitor's long term memory.

RESULTS

A typical experiment for one analyte used in this evaluation, TCE, is illustrated in Figure 1. A total of six concentrations (1 - 32 µg/g of soil), were tested on one day. Three spiked samples at each concentration were purged into Tedlar™ bags, and three readings were taken for each bag. These results show that replicate samples and replicate measurements from each sample are reproducible. The figure further illustrates that the test analyte does not interfere with readings for other analytes; that is, the monitor does not read TCE in the chloroform, PCE, carbon tetrachloride, or acetone channels. Similar experiments and observations were made with all the analytes.

The linearity of the method from 1-2 µg/g to 64-128 µg/g was very good. When theoretical concentration is plotted versus determined concentration, R^2 values are >0.99 for each analyte. The linear range of the instrument probably goes quite a bit higher, and may only be limited by the solubility of the analytes in the water extraction matrix. The slope of the theoretical versus determined concentration line indicates the accuracy of the method, assuming that >95% of the analyte is purged under experimental conditions. The accuracy of chloroform, TCE, and carbon tetrachloride measurements was good - 87%, 88%, and 87%, respectively. Only about 5% of the acetone spiked into soil samples was purged under these experimental conditions and no interference was observed with the detection of any of the other analytes.

Problems were encountered with accurately preparing a 25 ppm spiking solution of PCE in water. Analysis by GC/MS indicated that the actual concentration of a 25 ppm standard using our preparation method was 20 ppm. When determined PCE concentrations are compared to theoretical concentrations based on a 25 ppm spiking solution, accuracy appears to be 65%; however, when compared to theoretical concentrations based on a 20 ppm spiking solution, accuracy is 82%. The nature of the difficulty in accurately preparing PCE standards in water needs further investigation. The multi-gas monitor, however, seems capable of measuring the PCE present in the spiking solution.

The ability of the multi-gas monitor to cross compensate for interference among compounds was investigated by analyzing mixtures of four VOCs at variable concentrations. The results of that experiment are presented in Table 1. Compensation was effective; mean results for analytes in the mixtures were between 89% and 117% of the concentrations found when each analyte was determined separately.

DISCUSSION

The method is accurate, linear, and reproducible for a number of VOCs. Minimal training is required to operate the monitor, and samples can be analyzed rapidly - two people can easily run at least 30 samples in one day. Multiple analytes can be measured simultaneously in a single sample, and a large variety of analytes can be analyzed through the use of appropriate optical filters. Record keeping is convenient, especially if a printer is available to keep a running log of measurements. The instrument is portable, and can be powered by a generator or a converter attached to a car battery. The primary limitation of the method is that analyses are susceptible to interference from contaminants the instrument is not set up to monitor and compensate for. This method is probably not sufficiently sensitive that regulatory decisions could be made based on the results obtained. A good application of this method would be to monitor sites where the contamination profile is known, and to follow the results of remediation efforts.

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Table 1. Percent of expected analyte concentration found in the investigation of the ability of the multi-gas monitor to cross compensate when analyzing mixtures of VOCs. "Levels" are: High, 60 µg/g of soil; Mid, 15 µg/g of soil; Low, 3 µg/g of soil.

Mean Results for Twenty Mixtures

Chloroform	TCE	PCE	Carbon Tetrachloride
117.5%	97.0%	100.6%	89.0%

Individual Results for Each Mixture

Mixture #	Chloroform	TCE	PCE	Carbon Tetrachloride	Mixture #	Chloroform	TCE	PCE	Carbon Tetrachloride
1	88.3%	67.2%	83.3%	78.9%	11	104.3%	103.0%	101.2%	105.7%
Level	High	Low	High	Mid	Level	Mid	Mid	Mid	Mid
2	176.4%	95.9%	98.3%	98.5%	12	99.9%	94.7%	92.7%	76.0%
Level	Low	High	High	Mid	Level	High	High	High	Low
3	75.2%	108.5%	114.2%	107.8%	13	154.9%	107.5%	90.1%	69.4%
Level	Low	Low	Low	Mid	Level	Low	Low	Mid	Low
4	102.9%	95.0%	99.1%	101.7%	14	116.1%	93.6%	92.1%	95.3%
Level	Mid	High	High	High	Level	Mid	Mid	High	Mid
5	117.6%	108.1%	110.7%	102.5%	15	117.3%	94.9%	92.4%	64.8%
Level	Mid	Mid	Mid	Mid	Level	Mid	Low	Mid	Low
6	102.6%	103.8%	138.3%	106.0%	16	113.7%	90.3%	93.8%	66.6%
Level	Mid	High	Low	Mid	Level	Mid	High	Low	Low
7	170.1%	107.0%	100.8%	82.5%	17	99.5%	91.9%	98.6%	94.5%
Level	Low	Mid	High	Low	Level	High	High	Mid	Mid
8	112.2%	99.2%	97.0%	97.2%	18	101.5%	105.0%	92.3%	84.1%
Level	Mid	Low	High	High	Level	High	Low	Low	High
9	133.6%	98.4%	110.1%	96.6%	19	157.9%	89.1%	96.3%	83.8%
Level	Low	High	Mid	High	Level	Low	Mid	Low	High
10	106.3%	100.1%	126.4%	85.7%	20	99.5%	87.8%	84.5%	83.1%
Level	High	Mid	Low	Low	Level	High	Mid	Mid	High

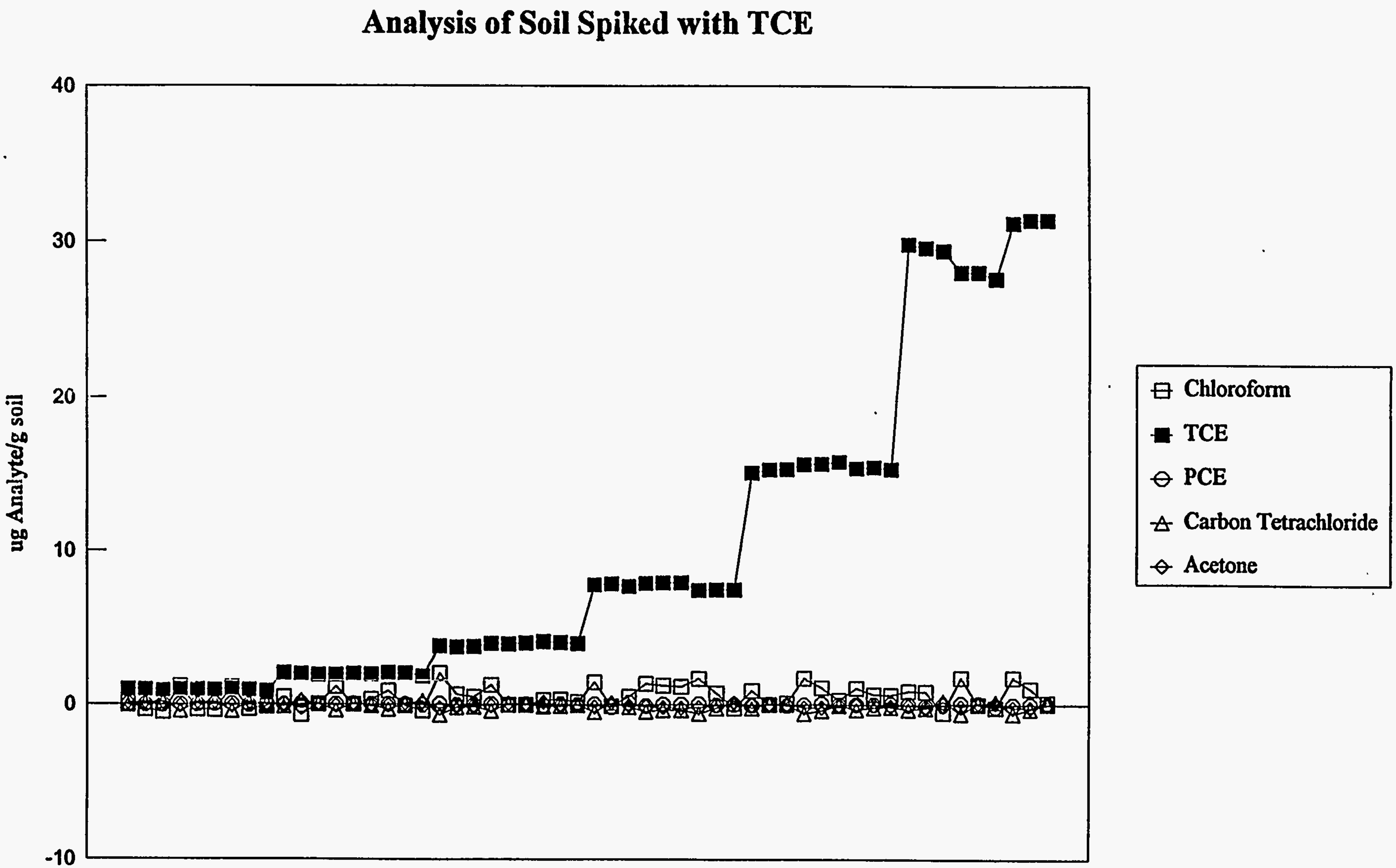

Figure 1. Typical analysis of TCE spiked soil. Soil samples were 5 g and contained TCE at concentrations from 1 - 32 μg/g of soil. Three soil samples at each concentration were analyzed, and three measurements were taken per sample.