

## Introduction

Defiant's FROG-4000™ is a portable GC-PID whose rugged design enables it to easily analyze water, soil, and air for VOCs. In this case study we investigate the FROG's effectiveness at analyzing water for ethylene dibromide (EDB). At the end of the study we measured several replicate samples to statistically determine the method detection limit. EDB was used as an anti-knock agent in leaded fuel and it was formerly used as a pesticide. As such, EDB made its way into surface water through runoff and into groundwater by leaching through leakage from use, storage, or transportation of leaded gas.

## The FROG-4000™ Portable GC System

The FROG-4000™ seen in Figure 1 is the smallest portable GC/PID system on the market today. Using a MEMS preconcentrator coated with a designer nanomaterial and micro fabricated GC column, the FROG-4000 can achieve the same detection limits of a traditional bench top GC system at fraction of the cost and size.

One of the principal strengths of the FROG-4000 is its ability to analyze samples in the field without the complications like refrigerated storage, overnight shipping, and exorbitant fees for quick results.

A computer is only required for calibration. Intuitive software facilitates the calibration process. Once the calibration parameters are loaded into the FROG, the user no longer needs a computer. After the calibration has been

loaded into the FROG, it will report chemical name and concentration to its four line display. In addition, the chromatograms will be recorded on a built-in micro-SD card.

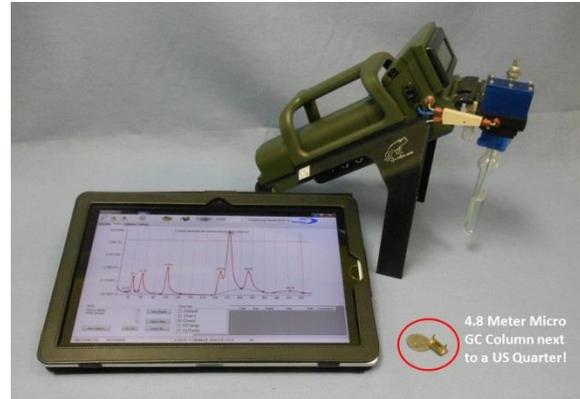


Figure 1: This is the FROG-4000™, the world's most portable GC system.

There are many difficulties encountered when using a traditional bench top GC in the field. They require compressed gas cylinders, a computer, and generator to be used in the field. Also, they require a separate piece of equipment called a purge and trap to extract VOCs from water or soil. A traditional GC weighs 60 pounds or more and it is usually found in a trailer when used in the field. The FROG-4000 has an integrated purge-and-trap for water and soil. It uses a pump with a scrubber to generate a clean carrier gas in the field. It is battery operated, weighs 4.8 pounds and its rugged design enables field personnel to use it anywhere.

A traditional GC can require up to an hour for each analysis. The FROG can perform an analysis on VOCs in five minutes, with the FROG-4000's 8-hour rechargeable battery that translates to more than 50 samples in the field!

The FROG used in this study contained the most sensitive PID and micro preconcentrator offered by Defiant. In addition, it contained a 4.8 meter column.

### Sample Collection Time

The FROG integrates two pieces of equipment into a seamlessly operating field system. The first is a microfabricated portable GC and the second is a purge and trap VOC concentrator. A purge and trap is a traditional means of stripping and concentrating VOCs from water or soil samples. In general, a water sample is placed in a sparge bottle. Next, air is percolated through the water sample to purge VOCs from it. That gas is directed through our preconcentrator where VOCs are trapped. The amount of time it takes to effectively strip VOCs from a sample can vary. For convenience, we have determined the optimum sample collection time for EDB. In our case study, we analyzed 4 replicate concentrations of EDB in water and varied the sample collection time with each replicate. Next, we compared the results from those analyses. Figure 2 shows the response from the FROG for each replicate sample. As can be seen in figure 2, the highest response was observed using a samples collection time of 60 seconds.

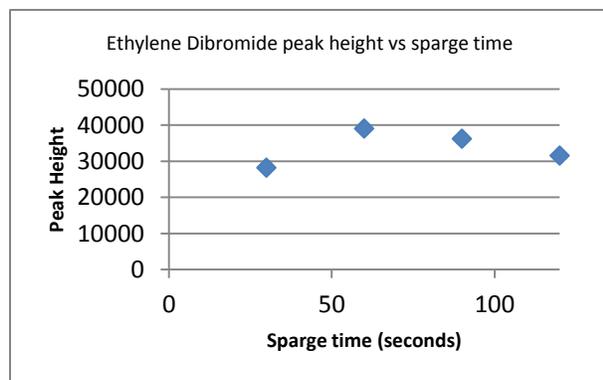
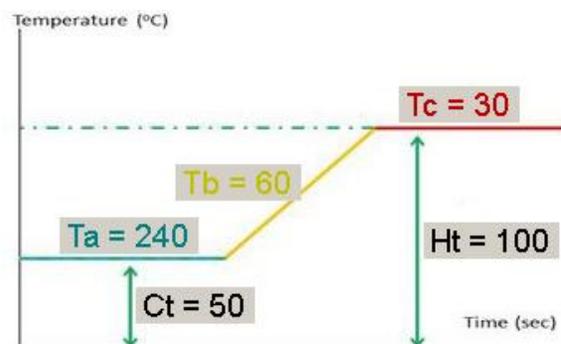


Figure 2 – EDB Peak height vs. sparge time

### Settings

The FROG-4000™ is user-programmable. The settings page in our software enables the user to develop their own method or to use established settings from case studies found at [www.defiant-tech.com](http://www.defiant-tech.com). Since the primary use of EDB was as an anti-knocking additive to fuels, we used settings that anticipate the presence of other chemicals that are associated with a fuel spill. BTEX is an acronym for benzene, toluene, ethylbenzene, and xylenes. This group of chemicals is a common signature associated with environmental contamination from fuels like gasoline or diesel. The settings listed below include the sample collection time we determined for EDB and integrate parameters to separate EDB from BTEX.

**Ta=240sec, Tb=60sec, Tc=30sec, Ct=50C,**  
**Ht=100C, Collect=60sec, Clean=4sec,**  
**Presettle=4sec, Settle=2sec, Fire=6 sec**



### Calibration

We prepared 5 standards at concentrations of 20, 40, 80, 160, and 200 µg/L of EDB in water. We used each of these standards to generate a calibration curve by performing a linear regression on the sensor response and standard concentration. Figure 3 shows the calibration for EDB on the FROG-4000.

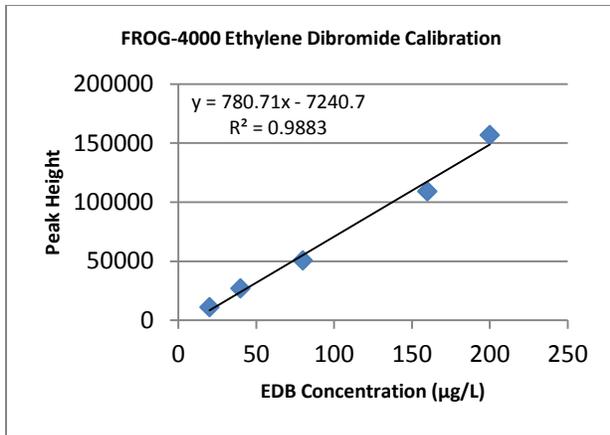


Figure 3 – Frog-4000 EDB Calibration

### Method Detection Limit

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. [1] We prepared and analyzed seven replicates at a concentration of 20µg/L. The table below shows the data for our MDL study. We calculated the MDL by multiplying the standard deviation of our seven replicate samples by the student's t value at 99% confidence interval.

Trial 1	17.98 µg/L
Trial 2	17.69 µg/L
Trial 3	16.20 µg/L
Trial 4	16.90 µg/L
Trial 5	19.41 µg/L
Trial 6	19.31 µg/L
Trial 7	18.41 µg/L
Standard Deviation	1.18
<b>Limit of Detection</b>	<b>3.72 µg/L</b>

Table 1 – Limit of detection results

### Discussion

The FROG-4000™ is capable of meeting quality control and quality assurance standards expected for purge and trap analysis of EDB using methods like EPA method 8021B. In the field, it may not be feasible to generate that quantity of data for field screening, site assessment, or guiding a cleanup effort. However, the FROG-4000™ is more than capable of producing quality data for making real time decisions in the field.

[1] 40 CFR Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11 Code of Federal Regulations - Title 40: Protection of Environment (2005)