



Defiant Technologies, Inc.

Analysis of High Concentrations of MTBE and BTEX in Soil and Solid Waste Samples

Application Note: Methanol Extraction of Soils, January 2013

The FROG-4000™ Portable GC System

Weighing less than 5 pounds, the FROG-4000™ (shown in **Figure 1**) is the smallest portable GC system on the market today. The FROG™ uses MEMS components and designer nanomaterials to deliver the same detection capabilities of a traditional bench top GC system but at a fraction of the cost and size. The FROG-4000™ is equipped with a purge-and-trap system for analyzing water and soil samples in the field.



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

In about 5 minutes, the FROG-4000™ can analyze water for VOCs and report the results to its display. The FROG's rechargeable battery provides up to 8 hours of usage in the field. A small pump in the FROG™ pushes ambient air through an inexpensive scrubber material to provide the carrier gas for analysis. There is no compressed gas cylinder, which minimizes the cost of operating the FROG™.

Introduction

The FROG 4000™ is a portable GC-PID system designed for detection of volatile organic compounds (VOC) in water, soil, and air. In this document we will focus on analysis of soils, specifically high concentrations of methyl tert-butyl ether (MTBE) and BTEX (that is, benzene, toluene, ethylbenzene, and xylenes) in soil.

The U.S. Environmental Protection Agency (EPA) recommends purge-and-trap for VOC analysis in soil; however, the sample preparation for purge-and-trap will vary depending on the concentration of the target analytes in the soil. There are two preparation methods for purge-and-trap; one is for high concentrations in soil and the other is for low concentrations. The EPA defines high concentration as samples containing VOC levels greater than 200µg of VOC per kg of soil. This unit measure is typically referred to as parts per billion (ppb). If the VOC levels are below that concentration then the user may place the soil directly in the sparging tube [1]. For the high concentration soil method, 5 grams of a soil sample is added to a pre-weighed VOA vial containing 10mL of a water miscible organic solvent, in our case methanol. [1] This technique is commonly referred to as methanol extraction. For the purpose of this application note we are performing the solvent extraction technique on a certified reference material, a soil that is spiked with MTBE and BTEX at known concentrations well above the 200ppb limit.

VOC Purge-and-Trap Basics

VOC analysis of soil and water using purge-and-trap is covered under EPA Methods 5035 and

5030, with accompanying references to Method 8021 for VOC analysis using a gas chromatographic column and photoionization detector (PID) [1], [2], [3]. In calibrating an instrument, known concentrations of analytes in water are tested with the instrument and a curve is produced that relates the analyte concentration to the chromatographic peaks measured by the PID. Typically five concentration levels are chosen that encompass the potential level of an unknown analyte. The purge time, effectiveness of sparging, and the ability of the preconcentrator to trap the analyte will all affect the results. As long as consistent practices are followed between the calibration and the actual sample tests, the results will be quite good. It may seem counter intuitive that calibrations performed on spiked water samples can be used to test soil samples, but this is an established practice that is presented in EPA Method 5035.

For concentrations below 200µg/kg, contaminated soil samples can be loaded directly into the sparge tube with 5 mL of distilled water, and the concentration results computed directly. For most soil matrices, the sparging agitation will be equally effective in driving VOCs from the soil sample as it was for the water sample. By loading 1 gram of soil into 5 mL of distilled water, the readings that were reported in ppb (that is µg analyte per L water) must be multiplied by 5 to obtain results in µg/kg for the soil. Simply stated, the PID produces a signal that is proportional to the mass of analyte it sees. If 5mL (= 5g) of spiked water sample used in calibration produces the same PID signal as 1g of soil, then the analyte concentration is 5 times higher in the soil. Similarly, if 0.8g of soil is used, then results reported by the instrument in ppb should be multiplied by 6.25 (=5 g/0.8g)

For higher concentrations of contaminants in soil, sparging will be less effective in removing the VOCs and Method 5030 recommends solvent extraction of the VOCs prior to purge-and-trap analysis. This effectively dilutes the sample VOCs in

a solvent, and makes them easier to sparge from water. The EPA recommends adding 5 g of soil to 10 mL of solvent, and then drawing a specified volume of the extract for analysis. As the concentration of contaminants increase, smaller volumes of the extract are used for analyses, therefore a dilution factor, *DF*, must be applied to the results to account for sample dilution. If the spiked water calibration results are in µg of analyte per L of water, and the volume of extract *V_{extr.}* is in µL, then the solid analysis results in µg analyte per kg of soil is

$$\frac{\mu g \text{ analyte}}{kg \text{ soil}} = DF \times \frac{\mu g \text{ analyte}}{L \text{ water}};$$

$$DF = \frac{5 \text{ g } H_2O}{5 \text{ g soil}} \cdot \frac{10 \text{ mL solv.}}{V_{extr.}(\mu L)} \cdot \frac{1000 \mu L}{mL} \cdot \frac{1 \text{ L } H_2O}{1 \text{ kg } H_2O}$$

Table 1 shows the EPA suggested extract volumes and the factors that relates ppb (µg analyte /L water) from the spiked water calibration to ppb (µg analyte/kg soil) from solvent extraction soil analysis.

Table 1: Injection Volume for Analysis

Approximate Concentration Range	Volume of Methanol Extract Injected in 5 mL clean water	DF, Dilution Factor to adjust for sample dilution
500 – 10,000 µg/kg	100 µL	100
1,000 – 20,000 µg/kg	50 µL	200
5,000 – 100,000 µg/kg	10 µL	1000
25,000 – 500,000 µg/kg	100 µL after 50:1 dilution of extract	5000
$DF = \frac{5 \text{ g } H_2O}{5 \text{ g soil}} \cdot \frac{10 \text{ mL solv.}}{V_{extr.}(\mu L)} \cdot \frac{1000 \mu L}{mL} \cdot \frac{1 \text{ L } H_2O}{1 \text{ kg } H_2O}$		

Calibration

Calibration of the FROG-4000™ was performed four days prior to analyzing our loamy clay soil spiked with MTBE and BTEX. We ran a five point calibration of spiked liquid samples ranging from 40 to 400µg/L. Each calibration standard was prepared in 5mL of deionized water. The FROG™ can hold a calibration for up to 3 weeks. We waited 4 days to analyze our certified reference material to demonstrate that its calibration is valid beyond the first day it was performed.

Sample Preparation

It is difficult to know when a sample contains a high concentration and the EPA recommends screening samples. They recommend that you start with a large dilution and work your way up to a more concentrated sample. Since our sample contains analyte concentrations well above 200µg/kg, we used methanol extraction.



Figure 2: This is a 20mL VOA vial containing our soil sample and the methanol used to extract it.

First, 10mL of purge-and-trap grade methanol was added to a 20mL VOA vial (shown in **Figure 2**). Then, the vial was capped and we determined its mass with an analytical balance. Next, we added 5 grams of our certified reference material, a loamy clay soil spiked with MTBE and BTEX. After adding the soil we measured the mass

of the vial with the soil to verify we had added 5 grams. [1] In the field, it may be convenient to use a portable balance like the ones shown in **Figure 3**.



Figure 3: These are two portable balances that would be suitable for use in the field. It is suggested to use a balance that can read to 0.01 g.

Keep in mind that every balance should be checked, and calibrated if necessary, with standard weights prior to use.

The vial was gently shaken for 2 minutes and allowed to rest so that the solid could separate from the methanol. **Table 1** shows the EPA's recommendation for the volume of methanol extract to inject into 5mL of clean water. As can be seen in the table, methanol extraction introduces a large dilution factor. This is why this technique is not recommended for concentrations below 200µg/kg. We injected 10 microliters into 5mL of deionized water for analysis. In the field it is convenient to use distilled water which can be purchased from a grocery store.

Results

We spiked 10 µL of our extract into 5mL of clean water. The sample we analyzed was a reference material and the concentration of each analyte in the soil was certified by the manufacturer. For Benzene, the FROG™ reported results of 20.4µg/L when analyzing the extract. When the dilution factor from **Table 1** is applied,

the final measured concentration of Benzene in the soil is calculated to be 20400µg/kg. **Table 2** below shows the certified values and the values determined by the FROG™. The final column in **Table 2** lists the % Recovery (%Rec). The equation for % Recovery is also shown below.

$$\%Rec = \frac{\{FROG\ Result\}}{\{Certified\ Value\}} * 100$$

The measured results are well within acceptable error limits for soil analysis.

Table 2: Reference Material Results

Analyte	FROG-4000™ (µg/kg)	Certified Concentration (µg/kg)	% Rec
MTBE	8900	9450	94%
Benzene	20400	20200	101%
Toluene	49300	51400	96%
Ethylbenzene	43700	40100	109%
p/m-Xylene	28900	30400	95%
o-Xylene	36300	33600	108%

A sample chromatogram is shown in **Figure 4**. The analytes are easily identified by the retention times (that is the time when the peaks crest) which line up precisely with the times reported for the calibration standards. The chromatogram also shows two later eluting peaks that probably resulted from naphthalene or methyl naphthalenes that were in the soil standard. If it is important to identify these compounds, subsequent calibrations could be performed with these compounds included in the standards.

Advantages

There are definite advantages in using the FROG™ over sending samples offsite. Sample holding time, offsite shipping, sample refrigeration are some of the issues. The FROG™ however had its results completed in the field.

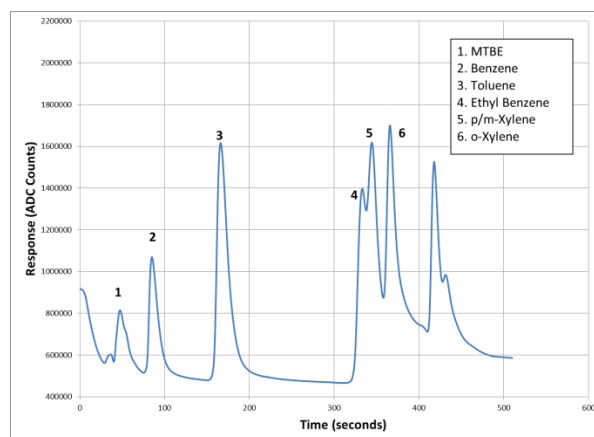


Figure 4: This is a chromatogram for the analysis of the loamy clay soil analyzed by the FROG 4000™.

Another advantage is that the FROG™ gives environmental consultants the ability to economically analyze a large number of samples in a short period of time. This enables a more thorough characterization of the site and environmental professionals get their results real time in the field so decisions can be made on the spot preventing further pollution.

Acknowledgements

Defiant Technologies would like to thank the EPA for their support via the SBIR program.

References

- [1] EPA Method 5035: Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, US Environmental Protection Agency, SW-846, December 1996.
- [2] EPA Method 5030: Purge-and Trap for Aqueous Samples, US Environmental Protection Agency, December 1996.
- [3] EPA Method 8021: Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors, US Environmental Protection Agency, December 1996.