### Introduction

Defiant's FROG-4000™ is a portable GC-PID (gas chromatograph photoionization detector) whose rugged design makes it perfect for use in the field. What distinguishes the FROG from other portable GCs is its ability to easily analyze liquid, solid, or air for VOCs. In this case study we explore the FROG's ability to determine the presence and concentration of diesel in crankcase oil. Diesel dilution in crankcase oil is a known issue that can be detrimental to an engine and to its components. The main issue with fuel dilution is a tremendous decrease in the viscosity of the lubricant. In general the lower viscosity the worse its lubricating power. When two fluids are blended, one with a viscosity of 100 centistokes and one with a viscosity of 1 centistokes, ill-effects can be noticed with just a few % of fuel dilution. This is a major concern for engines used in large earth moving equipment as well as diesel locomotives. Gas Chromatography is a reliable technique for measuring the amount of diesel that has contaminated the motor oil; however, conventional GCs lack the portability and convenience of the FROG-4000™. In this case study, our goal is to identify diesel intrusion into crankcase oil using the FROG-4000™and achieve a low limit of detection of 0.5%.

### 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 for extracting VOCs from water and soil samples in the field. Our MEMS components mimic the processes you are accustomed to with commercial analytical labs. The MEMS preconcentrator serves as the trap in our purge and trap and our micro GC column separates our analytes of interest. Detection is accomplished with a miniature photoionization detector.

One of the principal strengths of the FROG-4000 is its ability to analyze samples in the field without complications like refrigerated storage, overnight shipping, and exorbitant fees for quick results. In addition, since it is battery operated and scrubs its own carrier gas, it can be taken to remote locations to perform an analysis in real-time.



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

The FROG-4000™ is accompanied with our Ellvin™ software package. Ellvin™ is an intuitive piece of software that facilitates the calibration process, enables the user to adjust parameters, and watch data in real-time.  Ellvin™ is required for calibration,

however, once the calibration is loaded into the FROG, the user no longer needs a computer and the FROG will report chemical name and concentration to its display. Data collected in the field is recorded on a built-in micro-SD card.

The FROG's rechargeable battery provides up to 8 hours of usage in the field. Unlike other portable GC systems, the FROG does not require compressed gas cylinder to operate. A small pump in the FROG™ pushes ambient air through an inexpensive scrubber material to provide the carrier gas for analysis.

### 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. We have list the settings used for analyzing our extracts below. Since diesel is the analyte in question, we heated the GC to 130⁰C to ensure that any constituents of diesel amenable to purge and trap are completely eluted from the column.
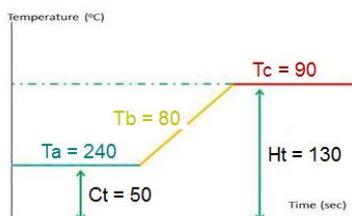


**Ta=240sec, Tb=80sec, Tc=90sec, Ct=50C, Ht=130C, Collect=30sec, Clean=4sec, Presettle=4sec, Settle=2sec, Fire=6 sec**

### Sample Preparation
Diesel fuel contains volatile organic compounds (VOCs) that are not present in motor oil. Our approach to determine diesel in crankcase oil will be to extract lightweight VOCs due to the diesel out of the oil. USEPA Method 5035 is a technique to extract VOCs from wastes using methanol. [1] The EPA has an accompanying guideline for analysis by purge and trap GC-PID method 8021. [2] Normally, a large amount of sample is extracted to achieve trace analysis of VOCs. However in our application the lowest concentration of interest is 0.5%. This is a massive concentration for GC analysis, therefore, we have modified this method both to simplify the extraction process and start with a large dilution of the oil sample.  We placed approximately 200mg of oil in a 7mL vial. Next, we added 4mL of methanol to the vial. Shaking the vial vigorously is enough agitation to extract VOCs from the oil. We allowed approximately 60 seconds for the oil to separate from our methanol extract. The oil mixture settles to the bottom and the methanol is the supernatant. An example of an extract is shown in figure 2 below. After extraction, a small 10µL of the methanol extract is injected into 5mL of water and analyzed by purge and trap GC-PID. VOCs are stripped from the water and trapped on our micro preconcentrator. They are thermally desorbed and analyzed by gas chromatography with a photoionization detector.
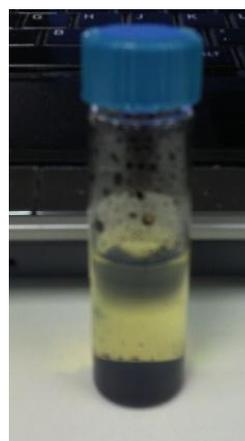


Figure 2: Above is a methanol extraction of motor oil contaminated with diesel.

### Calibration
We prepared 5 standards of diesel in motor oil at concentrations of 0.5%, 1.0%, 2.5%, 5% and 10% by volume. We purchased our diesel from a local

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station and motor oil (HD-30) from a local automotive store. Next, we extracted the standards using the technique described above. It is important to note that since our samples and our standards are extracted for analysis using the same technique, there is no dilution factor to apply. We chose the volumes used in our extraction technique to minimize sample preparation time and maximize convenience for the end user. Diesel is a refined material meaning it is really a large mixture of different chemicals spanning a wide range of boiling points. Ellvin™ has a feature that enables the user to integrate individual peaks or integrate over a range of peaks. We will choose to integrate a range of peaks to account for the fact that diesel is not a single chemical. For this case study, we integrated from 15 seconds to 250 seconds. Figure 3 is a screenshot from our Ellvin™ software. It shows the resulting calibration curve for diesel in motor oil.
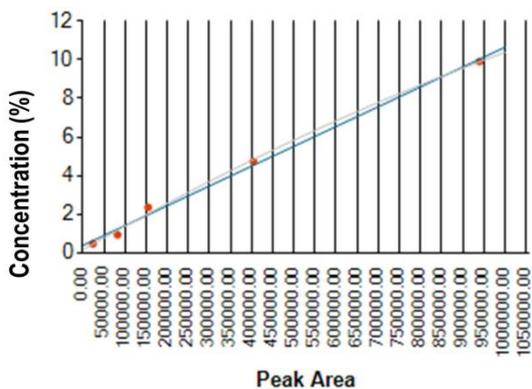


**Figure 3: Above is the calibration curve for diesel in motor oil.**

Figure 4 is a screenshot from our Ellvin™. The image shows the linear fit, quadratic fit, and the $R^2$ correlation for both fits. Both the linear and quadratic fits show good correlation. Our final concentrations are calculated using the linear fit.
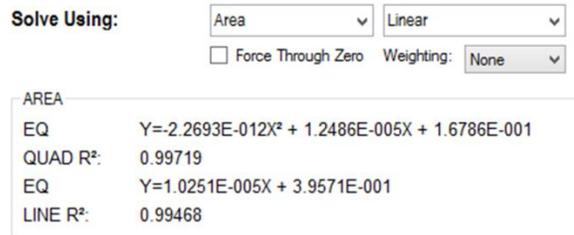


**Solve Using:** Area | Linear
☐ Force Through Zero  Weighting: None

AREA
EQ        $Y = -2.2693E\text{-}012X^2 + 1.2486E\text{-}005X + 1.6786E\text{-}001$
QUAD $R^2$:   0.99719
EQ        $Y = 1.0251E\text{-}005X + 3.9571E\text{-}001$
LINE $R^2$:   0.99468

**Figure 4: Above is the linear and quadratic fit for our calibration of diesel in motor oil. As can be seen from the $R^2$ values, there is excellent correlation.**

**Results**

We analyzed 3 samples of motor oil that were contaminated with diesel fuel. Our results are shown in the table below.

| Sample Number | % Diesel |
|---|---|
| 1 | 3.8% |
| 2 | 1.6% |
| 3 | 0.89% |

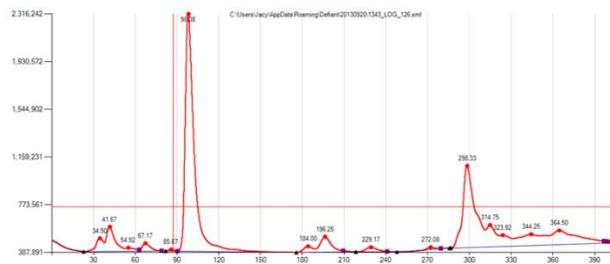Figure 5 shows a chromatogram from sample 1 in the table above.



**Figure 5: This is a chromatogram of sample 1.**

Figure 6 below shows a chromatogram of clean motor oil (HD-30) extracted with methanol. Figure 7 is the chromatogram of our extraction of motor oil spike to a concentration of 0.5% diesel. In addition to being the low level concentration on our calibration curve it is also our desired detection limit.
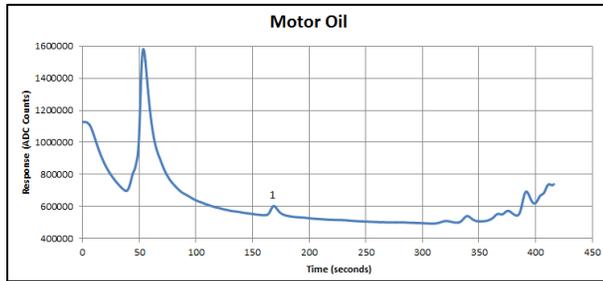
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**Figure 6: Above is an extraction of clean motor oil (HD-30) with no diesel fuel present.**

It is clear comparing the two chromatograms in figures 6 and 7 that there is a drastic difference in appearance.
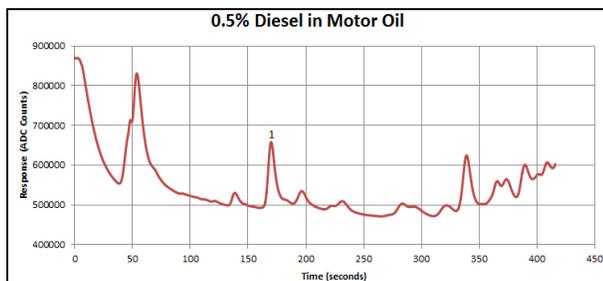


**Figure 7: Above is a standard of diesel fuel in motor oil (HD-30) spiked to a concentration of 0.5% by volume.**

In summary, our data shows that clean motor oil is drastically different in appearance from motor oil tainted with diesel. We have demonstrated that we can achieve a low limit of detection of 0.5% and our calibration demonstrates that we can expect linearity from the extraction and the analysis.

## Advantages

There are definite advantages in using the FROG™ over sending samples offsite. The FROG™ is ideal for this application because a gas chromatographic analysis can be performed in the field in real time. Receiving results in real time not only saves the cost of analysis and shipping, but can prevent further damage done to large expensive engines when the crankcase oil is contaminated with fuel.

Sample holding time, offsite shipping, sample refrigeration are some of the issues. Another advantage is that the FROG™ gives the users the ability to economically analyze a large number of samples in a short period of time. This will allow the user to trouble-shoot faster cutting down time of equipment.

## Acknowledgements

## 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 8021: Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors, US Environmental Protection Agency, December 1996.

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