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Ver.1 Rev. 1 04/09





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## Introduction to the PetroFLAG<sup>®</sup> Hydrocarbon Analysis System

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NOTE: PLEASE READ THE ENTIRE MANUAL BEFORE ATTEMPTING TO RUN THIS TEST

The PetroFLAG hydrocarbon analysis system is a broad spectrum field analytical tool suitable for any type of hydrocarbon contamination regardless of the source or state of degradation<sup>1</sup>. Unlike other field screening methods, the PetroFLAG system does not target specific compounds such as BTEX (Benzene, Toluene, Methylbenzene and Xylene) or PNAs (Poly-Nuclear Aromatics) that may be part of some hydrocarbon mixture. This makes the PetroFLAG system a very versatile analytical method that can be used on most hydrocarbon spills without prior knowledge of the BTEX or PNA content of the contaminant. The PetroFLAG system uses patented chemistry to respond to the broadest range of hydrocarbons possible. The PetroFLAG system is most sensitive to heavier hydrocarbons such as oils and greases and less sensitive to the lighter more volatile hydrocarbon fuels. The specially designed PetroFLAG analyzer allows the user to select, in the field, the response factor that is appropriate for the suspected contaminant at each site. The response factors for a number of contaminants are listed in Table 1. Using the selected response factor, the analyzer compensates for the relative response of each analyte and displays the correct concentration in ppm. The response curves for some typical hydrocarbon contaminants are plotted in Appendix A.

All chemical methods for hydrocarbon analysis in soil that are currently in use, whether they be field screening or laboratory methods, depend on solvent extraction to remove the hydrocarbons from the soil sample. The extraction efficiency for each method is a function of the solvent used and the extraction procedure. This efficiency is also dependent on

many other factors such as the soil type, water content, pH, etc. Many EPA SW-846 methods use chlorinated solvents or Freon as extraction solvents. These solvents were originally chosen for their extraction efficiency of polar organic compounds and may not be appropriate for hydrocarbons. Furthermore, special measures need to be taken with these lab methods when the soil is wet.<sup>2</sup> The extraction efficiencies may be as low as 1%<sup>3</sup> in some cases.

The extraction solvent used in the PetroFLAG system has been carefully developed to give consistent extraction efficiencies over the range of soil types and conditions most commonly encountered in the field. The PetroFLAG solvent system contains no chlorofluorocarbons or chlorinated solvents. The extraction efficiency is unaffected by soil moisture and, in most cases, is up to 15% (w/w).<sup>4</sup>

Because the PetroFLAG system has such a broad response spectrum, there are situations where it will indicate a higher hydrocarbon concentration than other methods. This can be due to the higher extraction efficiency of the PetroFLAG extraction solution or the broader response range of the detection system. SW-846 method 8015B, for example, targets only a very narrow range of

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<sup>1</sup>Brake fluid, phosphate ester based hydraulic oil, and other soluble fluids, will not be detected by the PetroFLAG system.

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<sup>2</sup>USEPA SW846 Method 3550A Ultrasonic Extraction Rev 1, November 1992

<sup>3</sup>Lee, W.E. III, Houchin, C.A. and Albergo, N., "TRPH Discrimination of Petroleum and Non-petroleum Organic Materials", *American Environmental Lab*, December 1993.

<sup>4</sup>The presence of water will cause a dilution effect resulting in a lower response. This effect can be corrected for, if the water content is known. (For a more complete discussion see "Using the PetroFLAG System: Effects of Soil Water Content on PetroFLAG Result")

hydrocarbons typically in the "Diesel" or "Gasoline" range (DRO or GRO). This method does not detect oils or greases unless the analyst changes the method and specifically looks for the heavier compounds. Requesting 8015B for diesel range hydrocarbons may result in under reporting of the actual total hydrocarbon contamination when oils or greases are present. Method 418.1 is a more general method and detects any Freon extractable compounds that contain a C-H bond. This method has relatively poor extraction efficiencies with many soil types. For a more complete discussion of the comparability of hydrocarbon methods see Appendix B.

Since the PetroFLAG system responds to the full range of hydrocarbons it will also detect some naturally occurring hydrocarbon-like compounds. (Method 418.1 uses a silica column to remove some of these compounds, but will still detect naturally occurring terpenes and creosotes, etc.) Therefore, in situations where high organic content is suspected, background levels outside the spill site should be determined. This will help to identify any naturally occurring sources of hydrocarbons that may cause a positive interference with the test. In cases where there exists a high natural organic background, a "Background Correction" can, in limited circumstances, be used to correct readings for this positive interference. Note: Because of the broad spectrum screening nature of the test, naturally occurring waxes and oils can cause high readings; however, false negatives or under-reported levels are very unlikely.

The PetroFLAG system is a valuable field analytical tool when used as part of a systematic sampling plan. As part of any site work, always have the hydrocarbon contamination characterized at some point during the project by for example, sending confirmation samples for closure to a certified laboratory. Since each laboratory method for petroleum hydrocarbons has a different target analyte and different response characteristics, use only appropriate methods for comparison. Furthermore, since the proficiency of laboratory methods for petroleum hydrocarbons varies from one laboratory to another; it is important to verify that the lab you use is proficient with the method you request. Always ask for QA/QC data and verify that the blanks, duplicates and spikes are within

specification for the method. When using a lab that is new to you, send them proficiency samples of known concentrations and varying water content.

Lab results often contain one or more samples that are designated "ND" (none detected) without a qualifier. This type of reporting is misleading because information on the limit of quantification is not included. The designation "ND" never means zero ppm and should be followed by an indication of the detection limits of the method used to obtain the result, e.g., ND<40 ppm. In many cases the detection limits for a method will vary with sample size, dilution factors or extraction procedures and may not be the same for all samples in the sample batch. The detection limits for some of the common lab TPH methods are on the order of 40-50 ppm. Therefore, when comparing laboratory data it is important to know the realized detection limits implied in any "ND" results.

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## Using the PetroFLAG System

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The PetroFLAG analyzer has been specifically designed to be used with the unique patented chemistry of the PetroFLAG system. The meter is shipped fully calibrated, preset with response factor 5. This calibration is sufficient to begin screening measurements; however, in order to achieve optimum performance we recommend that the analyzer be calibrated with each batch of samples, or at least daily. The PetroFLAG analyzer is easy to calibrate and a calibration standard is included with every refill pack.

The PetroFLAG analyzer stores two independent calibration equations in separate memory locations. Each calibration has a unique designation, "1C" or "2C". One way to effectively use this feature is to use one for a "low temp." calibration and one for a "high temp." calibration. This practice is very useful when working at field locations where the ambient temperature varies by more than 10°C over the course of the day. One calibration, run at the lower temperature in the morning, could be stored under "1C" and later as the temperature rises, triggering a temperature warning, a new calibration can be run and stored under "2C". (See below under "Temperature Effects")-

### Choosing the Correct Response Factor

The microprocessor in the PetroFLAG analyzer uses the calibration data to convert the optical reading into a preliminary concentration. The selected

response factor is then used to calculate the correct concentration for the analyte of interest. Therefore, it is important to choose the response factor that is appropriate for the particular hydrocarbon or class of hydrocarbons present at the site. The response factor can be changed at any time without affecting the stored calibrations. (See "Analyzer Operation Examples: Standard Operation- Changing Response Factor Without Recalibrating")

If the contaminant is known or suspected, choose the appropriate response factor from Table 1 and set that response factor on the analyzer. (See "Analyzer Operation" below.) If there is a mixture of hydrocarbons, use the most conservative response factor (i.e. the lowest) for the contaminants known to be present. If the contaminants are

unknown, choose a conservative response factor based on those hydrocarbons that are likely to be on the site. Examination of Table 1, indicates that the majority of typical contaminants are in response category 5 or above.

Table 1: Response Factors and Method Detection Limits for Common Hydrocarbons		
Hydrocarbon Type	Method Detection Limit (ppm)	Response Setting
Transformer Oil	15	10
Grease	15	9
Hydraulic Fluid	10	8
Transmission Fluid	19	8
Motor Oil	19	7
#2 Fuel Oil	25	7
#6 Fuel Oil	18	6
Diesel Fuel	13	5
Gear Oil	22	5
Low Aromatic Diesel	27	4
Pennsylvania Crude Oil	20	4
Kerosene	28	4
Jet A	27	4
Weathered Gasoline	200*+	2

\*See Appendix A

+Due to the non-linear response curve of Gasoline, quantification below 1000 ppm may underestimate the true contamination

## Analyzing High Concentration Samples

The PetroFLAG Hydrocarbon Analyzer is pre-programmed to warn the user of an over-range condition. If the over-range reading is outside of the linear range ( $\pm 10$  precision), but still within the quantifiable range ( $\pm 20\%$  precision), the reading will be displayed blinking. This reading can be used as an indication that the concentration in the sample is not less than the displayed value. Since the response curve for most analytes is non-linear at high concentrations, the concentration in the sample may be higher than the displayed value. If the over-range condition is outside of the quantifiable range of the meter, the display will show a blinking "EEEE". Either error indication can be cleared by simply inserting the next vial and pressing the <READ/ON> key.

Accurate results can be difficult to obtain when 10 gram soil samples with high contaminant concentrations are used since they may cause a over-range condition on the PetroFLAG analyzer. To quantify these high contaminant samples, extract fresh soil samples of 1 gram size and reanalyze. Then multiply the result by 10 to obtain the concentration in the sample. Using this procedure, it is possible to measure oils containing up to 50,000 ppm of light hydrocarbon contamination or 10,000 ppm of a heavier hydrocarbon. For readings at higher concentrations, a "high range kit" is available.

**NOTE:** The use of either smaller samples or "high range kits" will affect the precision and accuracy of the method as well as raise the MDL (Minimum Detection Limit) in proportion to the dilution factor.

## Converting Response Factors for Data Already Collected

Collected data can be easily converted to the correct reading when it has been determined that the wrong response factor has been used. To make this conversion, multiply the measured value by the response factor initially used to make the measurement and divide by the new response factor.

## Temperature Effects on Measurements

The PetroFLAG analyzer is equipped with an onboard temperature sensor to measure the ambient temperature while measurements are being made. The software uses the temperature readings to correct the optical readings for drift caused by the temperature fluctuations. The corrections have been determined for their effects on the turbidity development and the temperature drift of the electronics.

The PetroFLAG analyzer can be used at temperatures from 4°C to 45°C. The temperature corrections are valid for temperatures within 10°C of the calibration temperature. If a calibration is run with each batch of samples, the temperature correction is not significant and measurements can be made at any temperature within the usable range of the instrument. However, if no calibration is run and the ambient temperature deviates from the calibration temperature by more than 10°C, an error condition will result. The analyzer will display "Err4" which can only be cleared by pressing the <NEXT> key. Pressing of the <NEXT> key will clear the error and display the current reading. This reading can be recorded but it should be noted that the ambient temperature was outside of the acceptable 10°C window. Any other samples remaining in the series can be read, however, the same error condition will most likely occur. The meter must be recalibrated to eliminate this error condition.

The ambient temperature should be checked before starting to avoid a temperature error when a calibration is not run with the samples,. This can be

done by taking a reading without inserting a vial into the meter. If a reading is displayed, the temperature is within range and additional readings can proceed. If an error is displayed, the meter must be recalibrated before proceeding.

As previously mentioned, the storage of two calibrations, each at a different temperature, will reduce the number of recalibrations necessary as the temperature changes. If the two calibrations are stored under "1C" and "2C" and are run at temperatures levels 20°C apart, the effective temperature range for measurements now becomes 40°C.

### **Effects of Soil Water Content on PetroFLAG Result**

The presence of water in a soil sample will have a definite effect on the reporting value in the final PetroFLAG result. As with all field measurements, the PetroFLAG system result is calculated based on the sample weight "as received". If there is water present in the sample, this will produce a "wet weight" result causing an apparent under reporting by the PetroFLAG technique when compared to a laboratory reporting on a "dry weight" basis.

To correct for the difference between "wet weight" vs. "dry weight" results, simply divide the PetroFLAG value by the "fraction solids" (FS), where fraction solids is:

$$FS = \text{Dry Weight} / \text{Wet Weight}$$

or:

$$FS = (100 - \% \text{water}) / 100$$

Furthermore, when reporting the wet weight vs. dry weight results, the presence of water in a soil sample will cause a "dilution effect". Since the PetroFLAG solvent system is miscible with water, the water in the soil will be extracted into the solvent phase. The aliquot filtered into the developer vial will, therefore, be diluted by the presence of the water. To a first approximation, the correction for this "dilution effect" is made by multiplying the PetroFLAG result by one plus the "fraction water" in the sample,  $R' = R(1 + FW)$ , where fraction water (FW) is:

$$FW = (\text{Wet Weight} - \text{Dry Weight}) / \text{Wet Weight}$$

or:

$$FW = \% \text{water} / 100$$

The equation below can be used to achieve an overall correction that includes both the conversion of the PetroFLAG result to a "dry weight" value and the correction for the dilution effect:

$$R' = R((2/FS) - 1)$$

where:

R' = "Dry Weight" Corrected Result

R = Result displayed by PetroFLAG unit

FS = Fraction Solids

where:

$$FS = (100 - \% \text{water}) / 100$$

The above correction is applicable for typical soil types containing up to approximately 15% water by weight. For heavy clays or samples with higher water content, the effect of water content will vary with the analyte and should be determined specifically for each site.

In many cases, the effects of water content can be overcome by using a smaller sample size. This approach is the simplest and can be used effectively when a reduction in precision resulting from a smaller sample size still satisfies the overall data quality objective.

In some soils with high water content, the PetroFLAG response will be reduced both by the poor extraction efficiency of the analyte and a simple dilution. In these soils, the effect of water content on the extraction efficiency can sometimes be reduced by the addition of anhydrous sodium sulfate.

To treat such soils with sodium sulfate, weigh out the appropriate amount of soil sample (10 grams for a standard analysis) followed by the addition of up to 10 grams of anhydrous sodium sulfate. Mix the system thoroughly by stirring and/or shaking the sample until a free-flowing mixture is formed. Add the extraction solvent from a break-top ampule and then, follow the standard analysis procedure.

Treatment with sodium sulfate can improve the extraction efficiency, but will not correct for either the dilution effect or the wet weight/dry weight reporting error. The actual water content in the sample should be determined at some point so that the above corrections for wet weight and the dilution effect can be applied to the final result.

### Sample Preparation

Each 10-pack of soil reagents contains reagents and supplies for 10 tests. In addition, one blank and one calibration standard are included. Samples can be run individually or by batch. For optimum performance and throughput, samples should be run in groups of 10 samples, once the meter has been calibrated with a blank and a standard. The meter does not need to be recalibrated, provided that the operating conditions and reaction times are maintained. Total time to analyze 10-15 samples is approximately 20-25 minutes.

### Calibration

To insure accurate quantification and repeatable results, it is recommended that the PetroFLAG meter be recalibrated with each batch of 10 samples or, at least, daily. The meter is easily calibrated using an extraction solvent ampule as a blank and the calibration standard (supplied with each ten-pack of reagents).

After exiting the calibration mode, all additional readings made by the PetroFLAG analyzer will automatically incorporate the selected response factor. Therefore, rereading of the calibration standard will result in an incorrect reading unless the response factor being used is 10 and within the correct development time of the sample.

***NOTE:*** Once the *blank* and *calibration standard* have been read, discard them. They will fade with time and cannot be reused; **DO NOT USE THEM TO RECALIBRATE THE METER OR TO CHECK THE EXISTING CALIBRATION.**

### Preparing Blanks and Standards

The following description summarizes the procedure for preparing the blank and calibration standard.

Read the step-by-step instructions below completely before beginning the calibration process.

To prepare a *blank* and a *calibration standard*, first label two soil tubes, one as the "blank" and the other as the "standard". Add to the *blank* tube the contents of a break-top ampule labeled "Extraction Solvent". Add the contents of the break-top ampule labeled "Calibration Standard" to the *standard* soil tube. Process the blank and standard exactly as soil samples as described below. (See "The PetroFLAG Test Procedure")

### QA/QC

Performing periodic calibrations of the PetroFLAG meter is one of the most important quality control checks that can be made. In addition to calibrating the PetroFLAG meter, performance of periodic calibration also serves as a quality control check of the entire analysis system. Each time a calibration is performed the individual operator needs to prepare a fresh set of standards following the entire analysis procedure. To complete a valid calibration, the resulting test standards must meet the QC acceptance criteria stored in the meter. Each time a calibration is carried out, the meter verifies if the operator is performing the test correctly, e.g., following the correct order of steps in sample preparation, holding to the timing requirements, operating the meter correctly, etc. while the meter checks its basic operation. As each calibration is made, the intensity of the test solution is compared to the stored values for acceptance. If the optics have degraded or the electronics are out of specification the calibration will be flagged as an error.

The most important factor affecting the accuracy of PetroFLAG measurements is operator error followed by the ambient temperature determination. If the temperature varies by more than 10°C from the calibration temperature, the accuracy of the resulting measurement will be affected. Therefore, during each measurement made by the meter, the current ambient temperature is compared to the temperature determined at calibration. If the difference is more than 10°C, a warning is flashed alerting the operator of the temperature drift. This QC check is transparent to the user unless an error condition exists.



The internal check of the optical system is also transparent to the user. The PetroFLAG meter is designed with two independent optical channels. If, during a measurement, both channels do not agree, an error condition will be generated.

Along with these QC checks, which are performed automatically by the PetroFLAG meter, additional QA/QC procedures should be developed to provide assurances that the data quality objectives for each project are met. The most important part of any SOP (Standard Operating Procedure) should include provisions for ensuring that confirmatory samples are sent to a qualified lab for verification as to the type of hydrocarbon contamination present. This will also serve as a check of the response factor being used. When PetroFLAG meter results are determined to be either high or low when correlated to laboratory data, then a new response factor should be calculated and used. If the PetroFLAG results are not well correlated with the lab, then the field techniques should be examined to determine possible sources of error. A lack of correlation may be the result of inhomogeneous samples or may be due to splitting technique, etc.

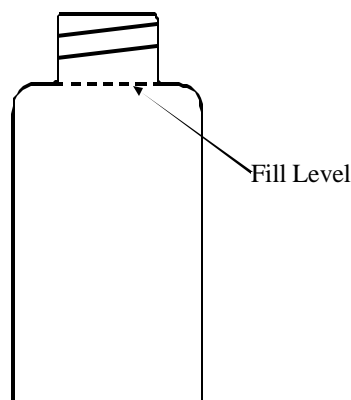
A program of field QA/QC should be developed that is compatible with the competing requirements of each user. It should include, a minimum of periodic soil blanks, equipment blanks, soil spikes, and dupes. Other procedures should be implemented depending on the specific requirements of each site.

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## The PetroFLAG Test Procedure

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- 1) Label the soil extraction tubes (plastic tubes with colored caps) and developer vials (small glass vials with black caps) with the appropriate sample ID. Use the self-adhesive labels to label the screw cap of the developer vial. Do not write in the center 1/3 of the developer vial as this may obscure the optical path when the readings are made
- 2) Weigh 10 grams ( $\pm 0.1$  gram) samples of all unknown soils into each of the labeled color-capped polypropylene tubes.
- 3) Set timer for 5 minutes. Add one break-top ampule of extraction solvent (blue polypropylene top) to the first tube. Start 5 minute timer and shake for 15 seconds. A separate ampule of extraction solvent is added to each of the remaining sample tubes when additional samples are being analyzed. Shake each tube for 15 seconds ensuring that the soil samples are fully wet. Shake each tube intermittently for a total of 4 minutes, then allow each tube to stand for the remaining 1 minute.
- 4) Verify that the filter disk is firmly attached to the syringe barrel. Remove the cap from the first labeled developer vial. Carefully decant the liquid from the polypropylene soil tube into the syringe barrel minimizing the transfer of soil particles, as this may plug the filter. Insert the plunger into the syringe barrel. Discard the first few drops from the filter into a waste container by pressing the plunger. Next, add the soil extract drop-wise to the developer solution until the meniscus just enters the neck of the vial (see figure). Shake the vial for 10 seconds, start the 10 minute timer and proceed to the next sample. Read the samples as close to the 10 minute time period as possible. Record this reading. Do NOT attempt to reread the sample as sample variation will occur due to fading of the solution over time. Do not let the developer vials stand longer than 20 minutes before reading, as this may result in lower than actual values.
- 5) If meter is off, turn on the meter by pressing <READ/ON> key and calibrate (optional, see Analyzer Operation).
- 6) To read, wipe the vial, place into the meter and press the <READ/ON> key. Be sure that the outside of the vial is clean before reading. Record result on work sheet. Read vials in the same order as they were prepared.



6 mL Developer Vial

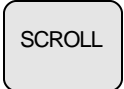

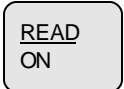
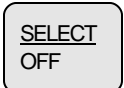
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## Analyzer Operation

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The PetroFLAG analyzer is controlled by a low-power consumption micro-computer with a pre-loaded operating program which is stored in EEPROM memory. The program cannot be lost regardless of battery condition. The meter stores two calibration curves in separate memory locations. These calibration curves can be independently updated and the response factors can be changed without losing the calibrations.

The PetroFLAG meter is configured to allow easy access to the program modes. The currently active mode is indicated on the LCD display while a reading is in progress. The response factor and the active calibration can be changed from the MAIN MENU using the four keys on the keypad. The four keys are:

	Scrolls through menu choices.
	Exits the read mode or skips a menu option without changing or executing. (Also used to clear error conditions.)
	Turns the meter on and starts a reading.
	Selects a menu choice. Manually turns meter off (only in the <i>read</i> mode).

When the PetroFLAG analyzer is turned on, the unit will return to the last mode it was in prior to being shut down. Under normal operating conditions, the analyzer will power up in the *read* mode. When the analyzer powers up in the *read* mode, the screen will display the last measured value for two seconds, and then, display the currently selected calibration curve ("1C" or "2C") and response factor (1-15). The meter is now ready to resume measurement. Simply insert a new sample vial into the meter and

push the <READ/ON> key. The display will initially indicate the calibration curve (either "1C" or "2C") and the response factor (1-15) that is currently selected. Next, the term "CALC" will flash on the screen and after 5 seconds, the measured concentration in ppm will be displayed.

**NOTE:** If the battery is disconnected and then reconnected, the meter will automatically return to the MAIN MENU. If the calibration curve and response factor displayed are the desired parameters, the MAIN MENU can be exited while retaining the calibration data by pushing the <NEXT> key. To return to the *read* mode, continue pressing the <NEXT> key until the display shows the calibration curve and the response factor continuously without blinking.

If you wish to exit the *read* mode, push the <NEXT> key and the operation is returned to the MAIN MENU. The <NEXT> key is also used to skip a step where a menu selection is required. To change a flashing menu option, push the <SCROLL> key while the option is flashing. To store the currently flashing menu choice, push the <SELECT> key. This stores the current choice and moves the flashing cursor to the next program mode.

### Selecting a Calibration Curve

Either of the two calibration curves, identified as "1C" and "2C", can be selected from the MAIN MENU. From either calibration curve any response factor can be selected. To change the response factor or to recalibrate the unit, use the <NEXT> key to enter the MAIN MENU screen. Immediately upon entering this menu three decimal points and the response factor are displayed. Next, the first two characters on the screen indicates the calibration curve that is currently selected ("1C" or "2C") is displayed. They will blink, indicating that a new curve may be selected. Use the <SCROLL> key to scroll to the next calibration curve. Push the <SELECT/OFF> key to select the curve.

The response factor will then blink. Use the <SCROLL> key to scroll to the desired response factor for the target analyte and press the <SELECT/OFF> key.

### Reading the Blank and Standard

After the response factor has been selected, the screen will read "CALC" for five seconds and then display the calibration temperature. This temperature will remain on the screen until either the <NEXT> key or the <READ/ON> key is pressed. The screen will then prompt you for the "blank" vial by displaying "-bL-". Insert the blank vial in the meter and press the <READ/ON> key (See "Preparing Blanks and Standards" under "Using the PetroFLAG Hydrocarbon Analysis System"). After 5 seconds the screen display should read "0" for 2 seconds. The screen will then prompt for the calibration standard, "-CSd". Insert the calibration standard in the meter, press the <READ/ON> key and after 5 seconds, the calibration is complete. The meter will then re-read the calibration standard to verify a valid calibration and display "1000". If the concentration of the calibration standard is not correct using the newly calculated equation, an error message will flash until the <NEXT> key is pushed. If an error condition exists, the previously stored calibration constants will be retained until a valid calibration is completed (See Appendix C, Table 1: Error Conditions).

### Taking a Reading

After calibration, the meter will then display the calibration curve in use ("1C" or "2C") and the current response factor selected. The meter is ready to read the first sample by inserting the sample vial into the meter and pressing the <READ/ON> key. After reading the sample, the meter will display the concentration in parts per million (ppm) until either the <READ/ON> key or the <NEXT> key is pushed. If no key is pushed for a period of five minutes, the meter will turn off automatically. If the meter turns off automatically, the meter can be reactivated by pressing the <READ/ON> key and the unit will return to the operation mode last used. The meter can be turned off manually by using the <SELECT/OFF> key, while in the *read* mode only.

The optical system on the PetroFLAG analyzer is covered with a screw cap to keep out stray light. To remove this screw cap from the vial holder, simply unscrew it 1/4 of a turn counter-clockwise. To make a measurement, insert the developer vial into the

unit, place the screw cap over the vial, and while pressing down on the cap (depressing the spring in the bottom of the vial holder), rotate the cap clockwise. Turn the cap until it is snug, but do not over-tighten.

### Power Requirement

The PetroFLAG analyzer is powered by one 9V alkaline battery (included). This battery should last for several thousand readings. If a low battery condition exists "LP" will appear on the display.

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## Analyzer Operation Examples

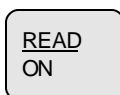
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Outlined below are step-by-step examples of how to use the PetroFLAG analyzer. Under normal operating conditions the meter will power up in the *read* mode. The examples given here categorized as "standard operation" assume that the meter was last operated in the *read* mode. If the meter was left in another mode for longer than five minutes or the batteries were removed, see below for special cases.

### Standard Operation:

(Whenever the last operation mode was *read*, the calibration data is current and the last-used response factor is valid.)

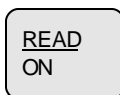
- 1) Turn the meter on by pressing:



The last reading will be displayed for 2 seconds. The display will show the calibration curve and response factor currently selected. The meter is now in the *read* mode.

- 2) Remove the screw cap, insert developer vial to be read and retighten cap.

- 3) To begin reading press:



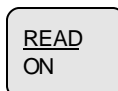
The display will show the calibration curve and response factor currently selected (blinking), the display will read "CALC" for 3 seconds, and the final result will be displayed.

- 4) The result will be displayed until the next reading is taken. To make the next reading: remove the vial and repeat steps 2 and 3 above.

### Standard Operation/Changing Response Factor Without Recalibrating:

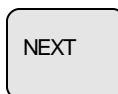
(Whenever the last operation mode was *read* and a different response factor is desired.)

- 1) Turn the meter on by pressing:



The last reading will be displayed for 2 seconds. The display will show the calibration curve and response factor currently selected. The meter is now in the *read* mode.

- 2) Return the operation to the MAIN MENU by pressing:



Three decimal points will be displayed along with the current response factor. The calibration curve designation will begin blinking.

- 3) The response factor entry mode is activated by pressing:



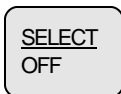
The response factor will begin to blink indicating that it may be changed.

- 4) Scroll to the desired response factor by pressing:



The next response factor will be displayed. Continue pressing the <SCROLL> key until the desired response factor is displayed. (Response factors scroll in descending order, i.e., 15-1)

- 5) When the desired response factor is reached, select it by pressing:



The new response factor has been selected. The meter will calculate and display the current temperature.

- 6) Move to the next screen by pressing:



The meter will prompt for the blank to be entered and the calibration procedure to begin by displaying "-bL-".

- 7) Skip this calibration procedure and move directly to the *read* mode, saving the new response factor but not recalibrating, by pressing (This exits the calibration mode without affecting the current calibration data):



The meter will display the current calibration curve and the selected response factor and is ready to read a sample using the new response factor.

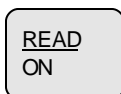
- 8) Proceed with the reading of a sample by following the above procedure for "Standard Operation" beginning at step 2.

#### Standard Operation With Recalibration:

(Where the last operational mode was the *read* mode and the meter is to be recalibrated.)

Prior to performing this calibration procedure, prepare the *blank* and *standard* as described in the manual under "Using the PetroFLAG Hydrocarbon Analysis System - Preparing Blanks and Standards". They may also be prepared along with the unknown samples in order to save time.

- 1) Turn the meter on by pressing:



The last reading will be displayed for 2 seconds. The display will show the calibration curve and response factor currently selected. The meter is now in the *read* mode.

- 2) Return the operation to the MAIN MENU by pressing:



Three decimal points will be displayed along with the current response factor. The calibration curve designation will begin blinking, indicating that it may be changed.

(If the displayed calibration curve is the one to be redetermined, skip directly to the response factor input by pressing the <NEXT> key.)

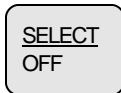
#### OTHERWISE

- 3) Scroll to the calibration curve that is to be redetermined by pressing:



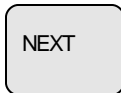
The display will show the next calibration curve designation.

- 4) When the desired calibration curve is determined, select it by pressing:



The calibration curve is selected and the meter will prompt for the input of the response factor.

- 5) If the response factor displayed is not the desired one, use the <SCROLL> key as described the previous section above under "Standard Operation - Changing Response Factor Without Recalibrating". If the response factor is correct, skip this step by pressing:



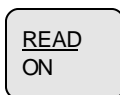
The meter will calculate and display the current temperature.

- 6) Move to the next screen by pressing:



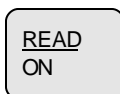
The meter will prompt for the blank to be entered and the calibration procedure to begin by displaying "-bL-".

- 7) Remove the screw cap and insert the prepared blank vial, replace the cap and begin calibration by pressing:



The display will blink showing the selected calibration curve and response factor. The meter will display "0" for three seconds and prompt for the calibration standard by displaying "-CSd".

- 8) Remove the screw cap and blank vial and insert the calibration standard vial. Read the calibration standard by pressing:



The display will blink showing the selected calibration curve and response factor. The display will read "1000" for three seconds and display the currently selected calibration curve and response factor continuously. The meter is now in the read mode.

- 9) Proceed with reading the unknown samples by following the procedure for "Standard Operation" above, beginning with step 2.

## Special Operating Conditions:

### Replacement of Battery:

**NOTE:** Use ONLY 9V Alkaline or 9V Lithium battery. Use of carbon/zinc battery will cause the PetroFLAG meter to malfunction.

Open the battery compartment by sliding the compartment door back (indicated by the arrow on the back of the unit). Lift out the old battery from the compartment and carefully unsnap the battery from the wire harness/connector. Replace with a fresh alkaline battery by snapping the wire harness/connector onto the new battery making sure the polarity is correct (The snaps will only go on one way). Reinsert the battery and connector into the compartment being careful not to twist/damage the connector wires. Replace compartment door by sliding the door forward until the latch clicks.

### Operation of the Meter After the Battery has been Disconnected:

When the battery has been disconnected the micro-processor will automatically return to the MAIN MENU once the battery has been reconnected. The meter, however, will not be in a *read* mode but is calibrated for use, unless other factors warrant recalibration. The operations to be performed will determine the exact steps to be followed. The steps to follow are described above in the various sections of "Analyzer Operation Examples."

### Meter Left to Turn Off in Other Mode:

When the meter is left in any "screen" for five minutes the meter will shut off automatically. The meter will return to last active screen when the <READ/ON> key is pressed.

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## Helpful Suggestions and Safety Precautions

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When PetroFLAG test results indicate no hydrocarbons are present, the sample can be sent in for certified laboratory confirmatory analysis. All environmental soil sampling used for final closure should be performed using methods that are approved by the local regulating agency.

Personal protection should be worn during soil sampling and testing. A minimum of latex gloves and goggles should be worn.

Decontamination stations should be set up using appropriate cleaners and rinsing solutions. Soil sampling equipment not supplied with the reagent pack should be decontaminated between sampling locations to prevent the possibility of cross contamination.

All reagents and sampling scoops supplied with the kit are single-use disposable items. Therefore, do not reuse spoons, tubes, filters, or vials. The electronic balance is *NOT* disposable.

Check ambient temperature BEFORE extracting soils, when a calibration procedure is not planned for the current batch of test samples.

Make sure the filter disks are screwed on tightly before adding the soil extract to a filter syringe.

Do not leave the PetroFLAG analyzer in direct sunlight when not in use. Store the instrument in the protective carrying case with the lid closed.

Make sure that the contamination at the site is characterized at some time during the investigation.

Avoid sampling organic matter. Scrape away organic material (leaves, sticks, etc.) before sampling.

Avoid sampling directly under pine, cedar, and fir trees unless the sample is collected below the organic layer. Do not collect samples from areas where tree roots have been encountered.

Avoid sampling directly beneath creosote bushes, sage brush and other oil bearing plants.

### Commonly Asked Questions

#### What are the response factors?

A response factor (RF) is the relationship between the analyte of interest and the calibration standard. The turbidity formed in the development solution by the sample is compared to the calibration standard followed by a calculation which determines the correct concentration for your contaminant. For Example: Equal concentrations of diesel and mineral oil do not produce the same level of turbidity. A RF value of 10 for mineral oil divided by the RF value of 5 for diesel produces a result of 2. This means that mineral oil forms twice the turbidity of diesel at the same concentration. Stated another way, 250ppm mineral oil forms the same turbidity as 500 ppm diesel. For more information please see Appendix A in the Manual.

#### Why doesn't my calibration standard read 1000ppm when I re-read it after calibrating?

This is directly related to the first question. The calibration standard is 1000 ppm mineral oil, therefore, if you read it on any RF other than 10 you will get a different number.

#### How long are my samples good for after they develop for 10 minutes?

The PetroFLAG development process is a temporary reaction, therefore, readings should be taken right at the end of the 10 minute development period. The turbidity will continue to develop for period of time, after which the solution will begin to fade. Do NOT attempt to reread the sample as results may vary due to these changes in the solution. No measurements should be taken after 20 minutes. This means you must record your data as it is generated because you cannot save your sample vials for future analysis.



## Caution

### **After I prepare a set of calibration solutions how long are they good for?**

Since the PetroFLAG development chemistry fades over time they are only good for a single use and the 10 minute time window should be adhered to.

### **The screen is displaying an error code, what does it mean?**

See the reference table in Appendix D for a list of “Error Conditions”.

### **What can I do if my reading is over-range?**

Process a new sample using a 1 gram soil sample and multiply the end result by 10. This sample dilution will allow you to read up to 10,000-15,000 ppm on most samples (1-1.5%).

### **The meter is “stuck” in the calibration program mode with the “1C” or “2C” characters flashing?**

The meter will not allow normal calibration procedure or sample measurement when the <READ/ON> key is pressed, but returns to a flashing “1C” or “2C” screen. This is usually caused by use of a non-alkaline battery. Replacement with a fresh 9V Alkaline battery should eliminate the problem and the meter should return to normal operation.

When opening the break-top ampules *DO NOT* remove the plastic sleeve from the top. It is there for your protection. Removing it may result in personal injury.

The Extraction Solvent and Calibration Standards contain methanol and are Flammable and Poisonous.

Wear rubber gloves and safety glasses while performing tests.

Dispose of all used reagents and soil properly.

Read the Material Safety Data Sheet before performing test.

## Manufacturer's Warranty

The reagents and supplies used in the PetroFLAG test are warranted to be free of defects in material and workmanship until the expiration date stamped on the box. Manufacturer's sole and exclusive liability under this warranty shall be limited to replacement of any materials that are proved to be defective. Manufacturer shall not be liable for any incidental or consequential damages.

Reliable test results are highly dependent upon the care with which the directions are followed and, consequently, cannot be guaranteed.

## Appendix A: PetroFLAG Response Curves

Most fuels, lubes and greases are complex mixtures of various hydrocarbons having a broad range of physical and chemical properties. The PetroFLAG system will detect a majority of the ecologically important hydrocarbon mixtures. The PetroFLAG responses to some typical hydrocarbon contaminants are plotted in figure 1<sup>5</sup>.

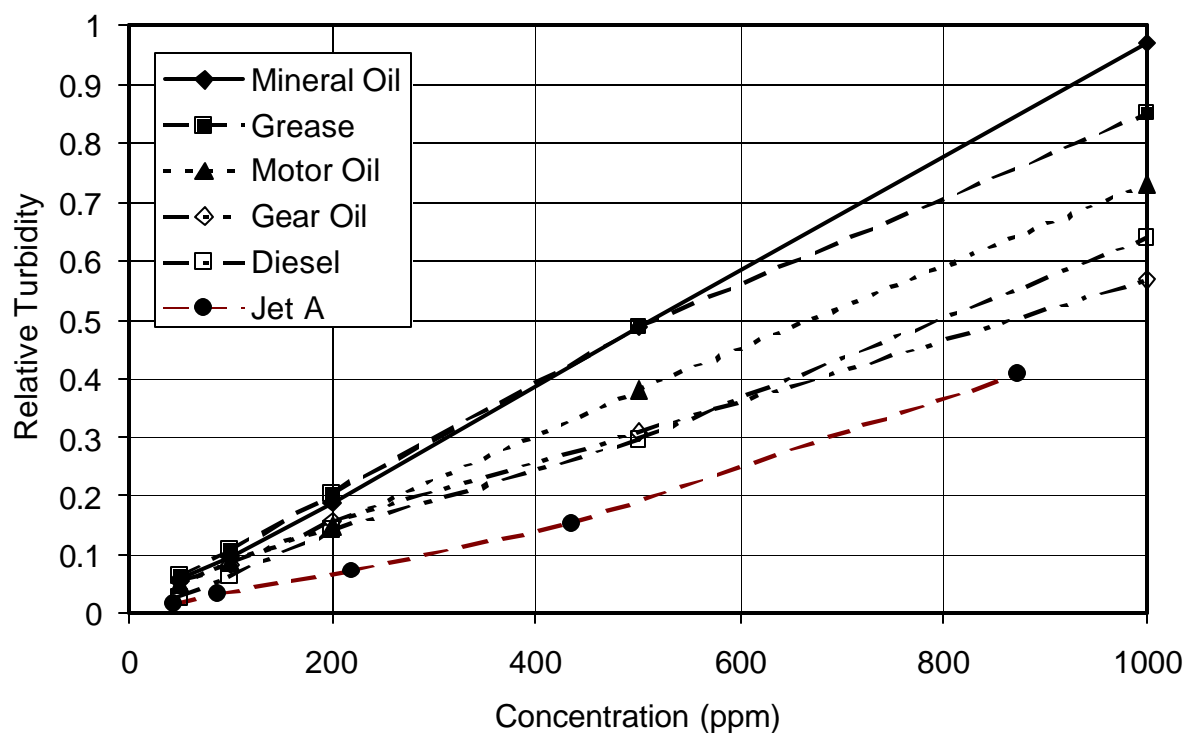


Figure 1: Relative Intensity Data for Common Analytes

<sup>5</sup>The lower limit of quantification, using a 10 gram sample size, is 1000 ppm for gasoline (linear range from 1000 ppm to 5,000 ppm). Brake fluid, phosphate ester based hydraulic oil, or other water soluble compounds will not be detected by the PetroFLAG system.

## Appendix B: Comparison with Laboratory Methods

In field trials, the PetroFLAG system was used at sites contaminated with diesel fuel or with oil and grease. In both cases the PetroFLAG results correlated very well with EPA laboratory methods. Both EPA methods 8015B and 418.1 were used to analyze the samples from the diesel site. The resulting correlations were 89% and 92% respectively<sup>6</sup>. The samples from the oil and grease site were analyzed using EPA method 418.1 for soil. The lab results confirmed the PetroFLAG results with no false negatives and only 2 false positives (10%). When comparing the field results and the lab results for the field split samples, the correlation between the PetroFLAG data and EPA method 418.1 for the laboratory split samples was 90%<sup>7</sup>.

When comparing the PetroFLAG field results with laboratory results using EPA methods it is important to keep in mind that EPA laboratory methods for TPH are known to have variable extraction efficiency. The extraction efficiency achieved using EPA laboratory methods varies with soil type and moisture content. In addition, the degree to which moisture affects the extraction is dependent on how the individual laboratory is implementing the method. It is, therefore, important to verify that the lab used for comparison is performing the method properly and that the recovery is known.

Another important factor affecting laboratory confirmation analysis is the inhomogeneous nature

of soil samples. Whenever possible, homogenize samples using standard methods<sup>8</sup> before taking "splits" to send to the lab for confirmation.

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<sup>6</sup>Wright, Keith A., "Evaluation of a New Field Test Kit for Determining Total Petroleum Hydrocarbon Concentrations in Soil at a Site Contaminated by Diesel Fuel", Presented at the AEHS Conference on "Hydrocarbon Contaminated Soils", January 11-13, 1995, New Orleans, LA.

<sup>7</sup>Wright, Keith A. and Jermstad, David B., "Evaluation of a Rapid Field Analytical Test Kit for Assessing Hydrocarbon Soil Contamination", Presented at the "Third International Conference On-Site Analysis", January 22-25, 1995 Houston, TX.

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<sup>8</sup>See for example: Pitard, Francis F., Pierre Gy's Sampling Theory and Sampling Practice, Volumes 1 and 2, CRC Press, Inc., Boca Raton, FL, 1992).

## Appendix C: Determining the Response Factor for Hydrocarbons Not Listed in Table 1

The response factors listed in Table 1 are calculated from response curves similar to those in Figure 1 in Appendix A. The response factor is equal to the slope of the response curve multiplied by 10. The slope of the response curve for the analyte is calculated from the response of the specific analyte relative to the response of the calibration standard. The calibration standard has a slope of one and a response factor of 10 on the PetroFLAG meter. Multiplying the slope of a specific analyte's response curve by 10 yields the appropriate response factor for that analyte.

When a suspected contaminant is not listed in Table 1, there are a few methods that may be used to determine the response factor. The method used is determined by the information and facilities available. The most accurate method would be to replicate the data in Figure 1 for the specific analyte, and then calculate the response factor from the slope of the response curve.

Initially, prepare soil standards from a single homogeneous batch of clean soil spiked at a minimum of 5 different concentrations between 100 and 1000 ppm. (For light hydrocarbons, a higher concentration range can be used.) Next, analyze the soil standards in triplicate using a calibrated PetroFLAG meter set to a response factor of 10. Plot the results with the true spiked concentrations on the "X" axis and the meter readings on the "Y" axis. The slope of the regression line (least squares line) through the data points multiplied by 10 is the response factor that should be used for this analyte. To avoid a low bias and false negatives, round the resulting number down to the nearest whole number when selecting the response factor for the meter. This method can be used if either the contaminant is known or a sample of the neat product is available.

**NOTE:** When the soil used to prepare the spiked soil standards is not actually clean but contains some hydrocarbons, the curve will have a positive intercept. This result should not affect the calculated response factor provided that the highest

spiked standard does not read higher than 1000 ppm on the PetroFLAG meter.

When the contaminant is unknown and a sample of the pure product is not available, then an alternative method can be used. The PetroFLAG results, with the meter set to response factor 10, can be compared with laboratory results from split samples analyzed in triplicate. This method requires extreme care in the homogenizing of the bulk material and also, the preparation of the split samples. Improper sample preparation can result in errors of 100 to 200% or greater. To minimize the effects of this sample variation, as many samples as possible should be analyzed (greater than 20) and the concentrations used should be evenly distributed over the range of 100 to 1000 ppm. Once the data has been collected, plot the data as described above using the laboratory reference method results as the known concentration. The slope of the regression line multiplied by 10 is then the response factor.

**NOTE:** This method is not as precise as the spike method and any bias in the laboratory method will result in an error in determining this response factor. It is important to check both the laboratory method and the lab performing the analysis thoroughly before using it as the reference method. (See Appendix B)

If the facilities are not available to perform these tests contact Dexsil for advice.

## Appendix D: Error Conditions

Table 2: Error Conditions

Message	Cause	Solution
Flashing Concentration Reading [Applies to Unknown Measurements]	Over range condition.  Sample concentration outside of linear range.	Use smaller sample (1 gram recommended) and rerun.
Flashing "EEEE" [Applies to Unknown Measurements]	Sensor over range condition.  Sample concentration too high.	Use smaller sample (1 gram recommended) and rerun.
"Err0" [Applies to Calibration Mode]	Blank and Calibration Standard vials mixed up.  Blank or Calibration Standard outside of QC window ( bL too high or CSd too low).	Check calibration vials. Rerun and/or make up new ones.
"Err1" [Applies to All Modes]	Readings from the two optical channels do not agree.	Check vial and reread. If error remains, rerun using another vial.
"Err2" [Applies to Unknown Measurements]	Sample is reading lower than the blank, e.g., Calibration Blank soil unusually high background or not zero.	Recalibrate using true Blank soil.
"Err3" [Applies to Calibration Mode]	Blank or Calibration Standard outside of QC window (bL too low or CSd too high).	Recalibrate using fresh calibration solutions.
"Err4" [Applies to Unknown Measurements]	Absolute temperature difference between calibration and reading exceeds 10°C.	Recalibrate at current temperature.
"Err5" [Applies to All Modes]	Ambient temperature outside of operating range. (4°C - 45°C)	Remove meter and reagents to climate controlled environment to recalibrate/rerun.
"LP"	Low Power	Replace battery.

## Appendix E: Meter Specifications

A/D Resolution:	0.5 ppm		
Display Resolution:	1 ppm		
Precision:	Analyte Dependent From MDL to Max Linear Range (MLR) $\pm 10\%$ +5 ppm From Max Linear Range to Max Quantifiable Range (MQR) $\pm 20\%$		
Measurement Range:	10-10,000 ppm (linear range analyte dependent)		
Operating Temperature:	4°C to 45°C		
Quantification Limit:	Analyte Dependent	Approx.	Approx.
	Response Factor	MLR (ppm)*	MQR (ppm)*
	15	730	1,460
	10	1,000	2,000
	5	2,000	4,000
	2	5,000	10,000

\*Actual limits realized in the field are temperature and device dependent. PetroFLAG meter automatically warns user when each limit has been reached.

Program Storage: EEPROM

Calibration Storage: EEPROM

Display: 4 digit ½ inch seven segment LCD

Batteries: One 9V Alkaline (included) [Use only Alkaline or Lithium type]

Battery Life: Approx. 4000 measurements or 1 year (using a 550 mAh alkaline battery)

Dimensions: length=5.75" width=3.5" height=2"

Weight: 9.85 oz ( 280 g)