METHOD 8630

GASOLINE RANGE ORGANIC HYDROCARBONS IN WATER AND SOIL USING ULTRAVIOLET FLUORESCENCE (UVF) WITH SOLVENT EXTRACTION

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts formally trained in the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique, which a laboratory can use as a basic starting point for generating its own detailed standard operating procedure (SOP), either for its own general use or for a specific project application. Performance data included in this method are for guidance purposes only and must not be used as absolute quality control (QC) acceptance criteria for the purposes of laboratory QC or accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method uses ultraviolet fluorescence to determine the concentrations of Gasoline Range Organics (GRO) in the C6 to C10 carbon range, which includes BTEX (benzene, toluene, ethylbenzene, and xylenes) and other volatile petroleum hydrocarbons (VPH). Specifically, this method detects monoaromatic hydrocarbons only and does not detect polyaromatic hydrocarbons, including Diesel Range Organics (DRO) or other hydrocarbon ranges above the C10 carbon number.

1.2 This method can be used to quantitate hydrocarbons that are soluble in methanol, hexane, or other suitable solvents provided that the desired performance data can be generated.

1.3 This method is not appropriate for the quantitation of individual compounds, unless the contaminant in the sample matrix only contains one compound (e.g. benzene). In most cases, GRO contaminated samples contain many monoaromatic compounds which co-fluoresce with UVF instrumentation. If analyzing individual analytes is required, refer to Method 8000 or Volatile Petroleum Hydrocarbon (VPH) Methods for guidance.

NOTE: Fluorescence-based instruments are not sensitive to aliphatic hydrocarbons.

1.4 Choosing the appropriate calibration standard is dependent on the type or age of petroleum suspected in a sample. Results may be biased low or biased high depending on which standard is used for calibration and analysis. In general, GRO content in fuels and oils can vary considerably and include a large number of refined petroleum products (e.g. gasolines, diesel fuels) and unrefined petroleum products (e.g. heavy fuel oils, crude oils). Since GRO is typically used for underground storage tank (UST) releases, this method was developed using commercially available certified reference standards suitable for most UST applications based on historical performance data compared to laboratory GC methods. Unlike GC methods, since UVF does not quantitate hydrocarbons using retention times, is not sensitive to aliphatic hydrocarbons and cannot detect individual compounds, this method is intended for screening purposes.

1.5 This method is used with Method 8640 for Diesel Range Organics (DRO) analysis to evaluate Method 8650 for Total Petroleum Hydrocarbon (TPH), by adding the GRO and DRO concentrations in a sample together to report TPH. This method was validated by U.S. EPA for TPH measurement in soil. See Reference 1 in Sec. 16 for guidance. North Carolina Department of Environment and Natural Resources (NCDEQ) approved this method for soil analysis at petroleum sites, requiring GRO and DRO analysis be performed to report TPH. Regulatory guidelines from 2017 are shown in Figure 1. See Table 3 in Reference 2, Sec. 16 for updated guidelines.

1.6 Prior to employing this method, analysts are advised to consult the manufacturer’s instructions for additional information on QC procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this method is provided by the Environmental Protection Agency (EPA) as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives (DQOs) for the intended application

2.0 SUMMARY OF METHOD

2.1 Samples are extracted in solvent for analysis by UVF using the appropriate sample preparation procedures specified by each manufacturer’s UVF instrument or refer to Method 3500 for alternative sample preparation methods.

2.2 GRO in samples can be measured using UVF instruments fitted with appropriate excitation and emission optical filters and ultraviolet light sources. Sensitivity varies depending on types and quantities of monoaromatic hydrocarbons in a sample. In general, UVF is less sensitive to the lighter weight compounds (e.g. benzene) and more sensitive to the larger weight compounds (e.g. xylenes), with no sensitivity to polyaromatic compounds.

2.3 This method is intended for both laboratory and field use. Refer to Method 8000 for additional calibration and quality control procedures for further guidance. Use of surrogates and surrogate recovery analysis is not used with this method.

3.0 DEFINITIONS

Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences during sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on glassware cleaning.

4.2 Raw data from all blanks, samples and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and take corrective action to eliminate the problem. Subtracting method blank values from sample results is not permitted. If measured concentrations are suspected of being biased or false positive results for a sample, the laboratory should qualify the affected data or otherwise inform the data user(s) of any suspected data quality issues.

4.3 Contamination from carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the glass cuvette used for analysis must be rinsed with solvent between sample measurements. Fill the cuvette with solvent and test a blank to check for contamination. Rinse again with solvent or use a new cuvette if measurements are elevated.

4.5 Phthalates in plastic laboratory supplies can extract in solvent and elevate results. Use glass, plastics coated with polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP) or use testing supplies provided by the manufacturer.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section lists laboratory glassware and supplies used to develop this method. Other, alternative supplies not listed may be used. Refer to each manufacturer’s product for guidance.

6.1 Ultraviolet Fluorescence (UVF) spectrophotometer

An analytical system (e.g., fluorometer) equipped with a UV light source, excitation filter, emission filter, detector, and glass cuvette or sample cell. This includes fixed-wavelength fluorometers, multi-wavelength scanning fluorometers and laser induced fluorescence (LIF) technologies. The analyzer must be fitted with suitable components for the intended application.

6.2 UVF instrument configurations

The choice of components will depend on the analytes of interest, the expected concentrations, and the intended use of the results. Commercially available fixed-wavelength analyzers with configuration listed in this section were used to develop the method and are not intended to exclude the use of other instruments configured differently or that may be developed. Laboratories may use other UV light and optical filter components provided that the laboratories document method performance data that are appropriate for the intended application.

Configuration for GRO - Use a 255-nm LED, 254-nm mercury vapor lamp or similar UV light source at this wavelength, fitted with a 254-nm peak transmission narrow band excitation filter and a 280-nm narrow band emission filter. Use of square quartz glass cuvettes is required.

6.3 Data system

A computer system that allows the continuous acquisition and storage of raw data recorded by the analyzer. UVF instruments that do not have computer connection capability must, at a minimum, provide output of raw data (fluorescence response or voltage) and/or concentration to record manually.

6.4 Digital balance, 0.1-g capacity or lower.

6.5 High precision adjustable micro pipette, 25 µL to 250 µL capacity.

6.6 Soil extraction jars, 30 mL capacity, HDPE plastic with wide mouth screw cap.

6.7 Water extraction vials, 40 mL capacity with or without 5 mL graduations, clear glass, with PTFE-lined screw cap.

6.8 Storage vials, 5 mL capacity or larger, clear glass with PTFE-lined cap.

6.9 Syringes, 5 mL capacity or larger, glass or polypropylene plastic with Luer lock.

6.10 Syringe filters, 0.45 µm size, PTFE-lined plastic with Luer lock.

6.11 Graduated cylinders, 5 mL, 10 mL or higher capacity with 1 mL graduations, glass, or polypropylene plastic.

6.12 Volumetric flasks, 5 mL, 10 mL or higher capacity, glass.

6.13 Solvent dispenser or squirt bottle, PTFE or FEP lined solvent resistant plastic.

6.14 Tissue wipes, lint free, laboratory grade.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade HPLC solvents, at a minimum, should be used in all tests. Unless otherwise indicated, all reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where specifications are available. Other grades may be used, provided the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent leaching of contaminants from plastic containers.

7.2 Extraction solvents

This method has been validated using the solvents listed below. Samples should be extracted using a solvent system that gives optimum, reproducible recovery of the analytes of interest from the sample matrix, at the concentrations of interest. The choice of extraction solvent will depend on the analytes of interest and no single solvent is universally applicable to all analyte groups. Whatever solvent system is employed, including those specifically listed in this method, the analyst must demonstrate adequate performance for the analytes of interest, at the desired project-specific concentration levels. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Method 3500, using a clean reference matrix. Method 8000 describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

Matrix:	Solvent:	CAS No.
Soil, sediment, most other solid samples	Methanol, Methyl Alcohol or other polar solvents	67-56-1
Fresh or salt water, groundwater, other aqueous samples	Hexane, n-Hexane or other non-polar solvents	110-54-3
Oils, Fuels, Sludges, Wastes or Non-Aqueous Phase Liquids (NAPL)	Hexane or use methanol if appropriate	

<u>CAUTION:</u> Avoid using dichloromethane (DCM or methylene chloride) solvent for soil extraction and analysis. DCM may damage square cuvettes. Use hexane if a more powerful solvent is preferred. Keep in mind the moisture content in soils or sediments may inhibit extraction efficiency with hexane.

7.3 Calibration standards – A minimum of five different concentrations for each parameter of interest should be prepared and used for instruments that can perform multi-point calibrations. If the instrument cannot, then calibrate using a single-point standard and a blank as indicated in Sec. 11.1.2. Calibration standards should be replaced after the manufacturer's expiration date or sooner if comparison with check standards indicates a problem. See Method 8000 for additional information on the preparation of calibration standards. Use standards specified below. Consult with the UVF manufacturer for guidance.

7.3.2 Primary calibration standard – Use to establish baseline GRO measurement. Use a BTEX mixture, containing 6 compounds all at equal concentrations, for GRO measurement if the suspected source of hydrocarbons is weathered or degraded (e.g. from an old spill) or for heating oils, heavy fuel oils and crude oils with medium to high boiling point ranges >170°C. Use this standard by default to report GRO in samples if the source of hydrocarbons is unknown.

7.3.2 Secondary calibration standard – Use a certified 50% weathered gasoline, CAS# 8006-61-9, formulated from a regular, unleaded gasoline fuel source, with a low boiling point range of 60°C to 170°C, as defined in Method 8015, Sec. 1.2.2. Use for GRO analysis if the suspected source of hydrocarbons is fresh and not weathered (e.g. from a recent UST spill) or for light-refined hydrocarbons (e.g. gasoline and jet fuels). These contaminants and the weathered gasoline standard contain a lower composition of aromatic hydrocarbons and fluoresce weaker compared to the BTEX standard. As a result, when used to calibrate, the 50% weathered gasoline standard produces higher sample readings and will perform better if results are biased low using the BTEX standard. Choose a CRM which produces sample readings 1.5 to 2 times higher compared to the baseline GRO measurement.

7.3.3 Project-specific calibration standard – Use alternative standards when appropriate, including GRO standards supplied by proficiency testing providers to perform GRO proficiency studies, for calibration and analysis.

7.4 Blanks – Three types of solvent blanks are necessary for analysis: (1) the calibration blank, which is used in establishing the calibration curve; (2) the method blank, which is used to monitor for possible batch contamination resulting from the sample preparation procedure; and (3) the rinse blank, which is used to flush the cuvette between all samples and standards. See Sec. 11.6 for frequency for analyzing rinse blanks.

7.5 As with the equipment and supplies, each commercially available testing product will supply or specify the reagents necessary for successful completion of the test. This includes the calibrators (standards) and solvents to use. Detailed information on reagent requirements is given in the manufacturer's literature. Store all reagents and standards according to the manufacturer's instructions, and, where applicable, discard any that are past the expiration date assigned by the manufacturer.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Sample collection, preservation, and storage requirements may vary by EPA program and may be specified in a regulation or project planning document that requires compliance monitoring for a given contaminant. Where such requirements are specified in the regulation, follow those requirements. In the absence of specific regulatory requirements, use the following information as guidance in determining the sample collection, preservation, and storage requirements.

8.1 See the introductory material to Chapter Four, "Organic Analytes" for storage conditions and holding times.

8.2 Store the sample extracts at ≤6 °C (protected from light) in glass vials equipped with PTFE-lined screw caps.

9.0 QUALITY CONTROL

9.1 General Guidance

Follow the manufacturer's instructions for the quality control procedures specific to use of the testing product. Also, refer to Chapter One for additional guidance on quality assurance (QA) and QC protocols that may be applicable. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a

Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those implementing the project and assess the results.

Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. Development of in-house QC limits for each method is encouraged as described in Sec. 9.5. Use of instrument specific QC limits is encouraged, provided such limits will generate data appropriate for use in the intended application. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to Method 8000 for specific determinative method QC procedures. Refer to Method 3500 for QC procedures to ensure the proper operation of the various sample preparation techniques. These methods were developed for gas chromatography analysis, but apply with this method in some cases. Some QC procedures may not be practical for use in field. Use for guidance purposes only.

9.3 Initial demonstration of proficiency (IDP)

The initial demonstration of method proficiency must be performed by the laboratory prior to independently running an analytical method, and should be repeated if other changes occur (e.g., instrument repair, significant change in procedure, and change in analyst). Refer to Method 8000 Sec. 9.0 for additional information regarding instrument, procedure, and analyst IDPs. An IDP must consist of replicate reference samples from each sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean reference matrix taken through the entire preparation and analysis.

9.4 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. The blanks should be carried through all stages of sample preparation and analysis. When new reagents or chemicals are received, the laboratory should monitor the preparation and/or analysis blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation, if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks need to be prepared for each set of reagents.

The laboratory should not subtract the results of the method blank from those of any associated samples. Such “blank subtraction” may lead to negative sample results. If the method blank results do not meet the project-specific acceptance criteria and reanalysis is not practical, then the data user should be provided with the sample results, the method blank results, and a discussion of the corrective actions undertaken by the laboratory.

9.5 Sample QC for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch of up to 20 field samples. Any method blanks, matrix spike samples, and replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.5.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair for up to 20 field samples. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on knowledge of the samples in the sample batch. If samples are expected to contain target analytes, laboratories may use a matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, then laboratories should use a matrix spike and matrix spike duplicate pair. Consult Method 8000 for information on developing acceptance criteria for the MS/MSD.

9.5.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked into a clean matrix with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike are not within control, the LCS results are used to verify whether this issue is due to laboratory performance or due to the matrix. Recovery issues in the LCS can indicate possible issues with the entire analytical batch. Consult Method 8000 for information on developing LCS acceptance criteria.

9.5.3 Also see Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for evaluating method performance should be developed using the guidance found in Method 8000.

9.6 Linear range

The linear range establishes the highest concentration that may be reported without diluting the sample. Following calibration, the laboratory may choose to analyze a standard at a higher concentration than the highest standard in the calibration. The standard must recover within 10% of the true value and if successful establishes the linear range. The linear range standards must be analyzed in the same instrument run as the calibration they are associated with (i.e. analyzed on a daily basis) but may be analyzed anywhere within that run. If a linear range standard is not analyzed for any specific analyte, the highest standard in the calibration becomes the linear range.

9.7 Lower Limit of Quantitation (LLOQ) check standard

The laboratory must establish the LLOQ as the lowest point of quantitation which, in most cases, is the lowest concentration in the calibration curve. LLOQ verification is recommended for each project application to validate quantitation capability at low analyte concentration levels. This verification may be accomplished by spiking either a clean control material (e.g., reagent water, solvent blank, Ottawa sand, diatomaceous earth, etc.) or a representative sample matrix, free of target compounds at the LLOQ and processing through all preparation and determinative steps of the method. Optimally, the LLOQ should be less than the desired regulatory action levels based on the stated Data Quality Objectives (DQOs).

9.7.1 Determination of LLOQs using spiked clean control material represents a best-case scenario and does not evaluate potential matrix effects of real-world samples. For application of LLOQs on a project-specific basis with established DQOs, a representative matrix-specific LLOQ verification may provide a more reliable estimate of the lower quantitation limit capabilities.

9.7.1.1 A LLOQ check standard (not part of an initial calibration) is prepared by spiking a clean control material with the analyte(s) of interest at the predicted LLOQ concentration level(s). Alternatively, a representative sample matrix may be spiked with the analytes of interest at the predicted LLOQ concentration levels. The LLOQ check is carried through the same preparation procedures as the environmental samples and other QC.

9.7.1.2 Recovery of target analytes in the LLOQ check standard should be within established in-house limits, or other such project-specific acceptance limits, to demonstrate acceptable method performance at the LLOQ. Until the laboratory has sufficient data to determine acceptance limits, LCS criteria having percent difference (%D) values of ≤20% may be used for the LLOQ acceptance criteria. This acknowledges the poorer overall response at the low end of the calibration curve. Historically-based acceptance criteria should be determined as soon as practical once sufficient data points have been acquired.

9.7.1.3 In-house acceptance criteria for recovery of the LLOQ check standard for a particular sample matrix can be calculated when sufficient data points exist. The laboratory should have a documented procedure for establishing in-house acceptance ranges; if the lower limit of the acceptance range is calculated to be <10%, it should be set to 10%. However, an alternative lower acceptance limit may be established by the laboratory or set at the project level through the DQOs in a QAPP.

9.8 Fluorescence quenching

Samples too high in concentration may quench or swamp the detector, producing low, non-linear measurements. This can occur when testing extracts without diluting the extract prior to analysis. Check for sample quenching by testing the extract at multiple dilutions, typically two or more as needed and multiply the readings by each dilution factor to compare the concentrations in the sample. Ideally, report sample results with readings between the LLOQ and the linear range of the calibration. Dilutions with readings below the LLOQ are too low and should not be used to calculate the final concentration. Dilutions with readings above the linear range are too high and are likely more susceptible to quenching. If the relative percent difference (RPD) between duplicates or percent relative standard deviation (%RSD) for more than 2 results is ≤20%, the average concentration of these results is reported as the final concentration in the sample.

NOTE: Heavy fuel oils, crude oils, coal tars or other samples high in PAH content will quench more than gasoline, diesel or other refined petroleum products low in PAH content.

10.0 CALIBRATION AND STANDARDIZATION

See Sec. 11.1 for information on calibration and standardization.

11.0 PROCEDURE

Set up the UVF with the proper optical configuration and calibration solutions following the manufacturer's instructions. Prepare calibration solutions in the same solvent used for sample analysis. Use the pipette, volumetric flasks, and glass storage vials in Sec. 6.0 to prepare stock solutions and calibration standards. Select and use commercially available Certified Reference Materials (CRMs) appropriate for analysis or use standards provided with each manufacturer's product, if available. Establish operating parameters that provide instrument performance appropriate for the intended application.

11.1 Initial calibration

11.1.1 For each analysis of interest, prepare Initial Calibration (ICAL) standards at a minimum of five different concentrations. One of the standards should be at a concentration at or below the LLOQ necessary for the project (based on the concentration in the final volume described in the preparation method, with no dilutions). The concentrations of the other standards should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

11.1.2 Calibrate UVF to a multi-point curve using the standards and a solvent blank following manufacturer's instructions. For instruments which can only perform a single-point calibration, use the highest concentration standard and a solvent blank to calibrate. Analyze the four other standards to record the response.

11.1.3 Record and calculate the calibration factors (CF) to establish the fluorescence response in the calibration curve. Fluorescence response may be voltage, raw fluorescence units (RFU), percent fluorescence scale (%FS) or other output from the instrument.

$$\text{Calibration Factor} = \frac{\text{Standard Response} - \text{Solvent Blank Response}}{\text{Standard Concentration}}$$

11.2 Calibration linearity

The linearity of the calibration must be assessed. This applies to both single-point and multi-point calibration curves.

11.2.1 If the percent standard deviation (%RSD) of the calibration factor is ≤20% over the working range, then linearity through the origin can be assumed, and the average calibration factor can be used in place of the calibration curve.

11.2.2 If the %RSD is >20% over the working range, linearity through the origin cannot be assumed. See Method 8000 for other calibration options that may be employed, which may include: a linear calibration not through the origin or a non-linear calibration model (e.g., a polynomial equation).

11.3 Calibration verification

Calibration check analyses are used to assess calibration drift and memory effects over time for each analytical system. Verification is accomplished by the measurement of a hydrocarbon standard on the calibration curve. These analyses may include a span (low and high) to cover the full calibration range, or mid-range concentrations using the ICAL standards or a Continuing Calibration Verification (CCV) standard made from the same stock solution as the ICAL standards. If reusing ICAL or CCV standards for analysis, pour back into glass vials after use and follow the manufacturer's instructions for storage and shelf life.

11.3.1 CCV standard must be analyzed in the beginning of each 12-hour analytical period prior to any sample analysis using the technique and conditions used for analysis of ICAL standards and samples.

11.3.2 Calculate the percent difference (%D) for the CCV standard response compared to the ICAL response. If the response is within ±20% of the response obtained using the initial calibration CF, then the initial calibration is considered still valid, and the analyst may continue to use the mean CF values from the initial calibration to quantitate sample results. If the response varies from the predicted response by more than ±20%, corrective action must be taken to restore the system or a new calibration curve must be prepared for analysis.

11.4 Second source standard

Prior to analyzing samples, verify the ICAL using a standard obtained from a second source to the calibration standards, if possible, such as a second manufacturer or a manufacturer's batch prepared independently from the batch used for calibration, if readily available. Suggested acceptance criteria for the analyte concentrations in this standard are 70 – 130% of the expected analyte concentration.

11.5 Laboratory control sample standard

LCS standards may also serve as the CCV and should be prepared and analyzed concurrently with the samples. Calculate the LCS concentration using the ICAL CF and if the response is within ±20% (or within 80 – 120% recovery) of the true value of the LCS, then the initial calibration is considered still valid, and the analyst may continue using the mean CF values from the initial calibration to quantitate sample results. If the response varies from the predicted response by more than ±20%, corrective action must be taken to restore the system or a new calibration curve must be prepared for analysis.

11.6 Solvent blanks

Solvent blanks or rinse blanks must be analyzed routinely before and after the CCV and prior to samples in order to ensure that the total system (i.e., solvent, cuvette) is free of contaminants.

11.7 Method blanks

Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment and laboratory supplies used in contact with the sample and reagents are assessed for background interference or contamination that exists in the analytical system that might lead to the reporting of elevated concentration levels or false positive data. Prepare the method blank using an interference-free blank matrix, similar to the sample matrix, to which all reagents are added in the same volumes or proportions as used in sample preparation. For aqueous analyses, analyte-free reagent water is typically used. For soil analyses, a purified solid matrix (e.g., sand) is typically used. Method blank results should be evaluated in conjunction with other QC information to determine the acceptability of the data generated for that batch of samples. The method blank results should be below the LLOQ for the target analytes being tested; otherwise, corrective action should be taken.

11.8 Water sample extraction and analysis

Add 15 mL of water to a 40 mL glass VOA vial. Add 15 mL hexane to vial to create a 1:1 extract. Tighten cap and shake by hand to mix contents for a minimum of 2 minutes. Let extract settle for several minutes to separate the hexane and water layers. If extracts are dirty and require filtration, use a syringe and syringe filter to remove particulates in the extract prior to use. If this is performed, QC samples in the analytical batch should also undergo filtration. Store filtered extracts in a glass extract vial. Pour the extract into a glass cuvette, clean the outside of the cuvette with a tissue wipe and insert into UVF for measurement. Prepare and test dilutions using the extract as necessary with a micro-pipette and volumetric flask or graduated cylinder.

11.8.1 Diluted extracts – Use more solvent with less water. Use 20 mL of hexane extracted with 10 mL of water to create a 2:1 diluted extract. Multiply sample readings by 2 to calculate final concentration in sample if diluted extract is used for analysis.

11.8.2 Concentrated extracts – Use more water with less solvent. Use 10 mL of hexane extracted with 20 mL of water to create a 1:2 concentrated extract or use 5 mL of hexane extracted with 25 mL of water to create a 1:5 concentrated extract. Divide sample readings by 2 or 5 to calculate final concentration in sample if concentrated extract is used for analysis.

11.8.3 Emulsified extracts – Allow extra time for the solvent and water to separate if solvent layer in extract is emulsified. Filtering the extract may be required to correct the problem or prepare a new sample using a diluted extract.

11.9 Soil sample extraction and analysis

Weigh sample into a 30 mL plastic jar or use a 40 mL glass VOA vial and add methanol using the weights and volumes listed below. Tighten the cap and shake by hand to mix contents for a minimum of 2 minutes. Let extract settle for several minutes afterward for solids to separate. Use a syringe and syringe filter to remove particulates prior to analysis. If extract is difficult to filter, prepare a more diluted extract. Pour the extract into a glass cuvette, clean the outside of the cuvette with a tissue wipe and insert into UVF for measurement. Store filtered extract in a glass vial. Prepare and test dilutions using the filtered extract as necessary with a micro-pipette and volumetric flask or graduated cylinder.

11.9.1 Undiluted extracts – Use 10-g (±0.1-g) of sample with 10 mL of methanol to create a 1:1 extract. If the undiluted extract is used for analysis, no dilution factor is applied to the final concentration. Prepare dilutions to the extract for analysis as needed.

11.9.2 2X Diluted extracts – Use 10-g (±0.1-g) of sample with 20 mL of methanol or use 5-g (±0.1-g) of soil with 10 mL of methanol to create a 2:1 diluted extract. Multiply sample readings by 2 to calculate final concentration in sample if diluted extract is used for analysis. Account for the 2X dilution factor when preparing additional dilutions for analysis.

11.9.3 4X Diluted extracts – Use 5-g of soil (±0.1-g) with 20 mL of methanol to create a 4:1 diluted extract. Use for clay or other highly absorbent soils which take a long time to settle and difficult to filter unless more solvent is used for extraction. Multiply sample readings by 4 to calculate final concentration in sample if diluted extract is used for analysis. Account for the 4X dilution factor when preparing additional dilutions for analysis.

11.9.4 10X or 20X Diluted extracts – Use for highly contaminated homogenous matrices, including sludges or oily samples. Use 2-g of sample (±0.1-g) with 20 mL of methanol to create a 10:1 diluted extract or use 1-g of sample (±0.1-g) with 20 mL of methanol to create a 20:1 diluted extract. Account for the 10X or 20X dilution factor when preparing dilutions for analysis.

11.9.5 Sediment samples – If samples are wet, the water content in the sample should be minimized prior to use. Decant water from the sample collection jar and use a 5-g or 10-g aliquot for extraction. If results are to be corrected for percent dry weight, use the leftover decanted sample contents for dry weight analysis.

11.9.6 Extraction time – Some matrices may require longer extraction time to improve extraction efficiency. Prior to filtering, allow sample to extract for 1 hour or up to 24 hours, periodically shaking the extract. This may not be practical when testing samples in the field.

11.9.7 Centrifuging extracts – May be used as an alternative to filtering extracts provided the extract is clear of particulates which may cause interference in readings.

11.10 Determination of percent dry weight

When sample results are to be calculated on a dry weight basis, a separate portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

CAUTION: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

11.10.1 Immediately after weighing the sample aliquot to be extracted, weigh an additional 5- to 10-g aliquot of the sample to the nearest 0.01 g into a tared crucible. Dry this aliquot overnight at 105 °C. Allow to cool in a desiccator before weighing.

11.10.2 Calculate the % dry weight as follows:

$$\%\ \text{dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}}\ \text{x}\ 100$$

This oven-dried aliquot is not used for the extraction and should be appropriately disposed of once the dry weight is determined.

11.11 Quantitation

The concentration of hydrocarbons in the sample is measured on the calibration curve and recorded by the instrument. Report sample readings within the linear range of the curve. When sample extracts are prepared and analyzed at different dilutions, the readings should have RPD or %RSD (comparing more than 2 replicates) ≤20%. Report the average concentration. If the RPD or %RSD in sample results is >20%, the sample may be quenching the detector or an error occurred preparing the dilution. The analyses should be performed again.

11.12 Instrument maintenance

Refer to each manufacturer's product for instrument maintenance instructions.

12.0 DATA ANALYSIS AND CALCULATIONS

See Sec. 11.11. Refer to the manufacturer's instructions regarding data analysis and data calculations. Results need to be reported in units commensurate with their intended use and all dilutions must be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data does not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. Performance data must not be used as absolute QC acceptance criteria for laboratory QC or accreditation.

13.2 In the case of this method (which may be used in either the field or the laboratory), any test kits used must be able to meet the performance specifications for the intended application. However, required performance criteria for a particular testing product may be included in the manufacturer's instructions.

13.3 Table 1 shows fluorescence of Certified Reference Materials (CRMs) used to establish baseline GRO measurement as specified in Sec. 7.3 and 11.4. Data performed by a single laboratory with analyzer configuration specified in Sec. 6.2, testing samples at 10 ppm concentrations using two calibrations. Calibration 1 was performed using Sitelab Corporation's GRO standard p/n CAL-025M in methanol, containing a 6 compound BTEX mixture all at equal concentrations. Calibration 2 was performed using AccuStandard, Inc. p/n GA-W50-10X, containing 50% weathered gasoline supplied in methanol. The two calibration standards contain different compositions of volatile hydrocarbons. In this case, the weathered gasoline standard fluoresces weaker compared to Sitelab's GRO standard. As a result, sample readings are always about 1.6 to 1.7 times higher or lower depending on which calibration is used. This ratio is within the range specified in Sec. 7.3.2. Other AccuStandard CRMs containing BTEX mixtures were analyzed and percent difference (%D) values are close to 100% compared to the Calibration 1 response. Alternative BTEX and 50% weathered gasoline CRMs made by Restek

Corporation were analyzed and fluoresced stronger in Calibrations 1 and 2, but ratios exhibited are within the 1.5 – 2x ratio limit and the two percent difference values meet the 70 – 130% acceptance limit, which qualifies these products as second source calibration standards. This data is provided for guidance purposes only.

13.4 Table 2 shows the fluorescence response of monoaromatic compounds using AccuStandard CRMs supplied in methanol comparing two calibrations used for analysis. Data performed by a single laboratory with analyzer configuration specified in Sec. 6.2. Fluorescence response was calculated by dividing sample readings by the concentration of the standard used and shown as a percentage. Response varies depending on the size and shape of each molecule and which standard is used for calibration. In this case, the weathered gasoline standard fluoresces weaker (58%) compared to Sitelab's GRO standard (100%) analyzed in Calibration 1. Sitelab's GRO standard fluoresces stronger (170%) compared to weathered gasoline (100%) analyzed in Calibration 2. This difference is exhibited in the sample results. This data is provided for guidance purposes only.

13.5 Table 3 shows the fluorescence response of gasoline range organics in a variety of fuels and oils exhibiting low to high GRO content. Data performed by a single laboratory with analyzer configuration specified in Sec. 6.2, using the same two calibrations in Table 1. Samples consisted of AccuStandard CRMs, Non-Aqueous Phase Liquids (NAPL) collected from oil recovery wells from different sites, light crude oil using a Standard Reference Material (SRM) from National Institute of Standards & Technology (NIST) and other samples collected from retail stores or manufacturers for comparison. No. 6 fuel oil, transformer oil, crude oil and NAPL samples were supplied in hexane with standards prepared in methanol for analysis. Gasolines, diesels, aviation fuels and other light-refined fuel oils were supplied in methanol with standards diluted further in methanol for analysis. Chemical Abstract Service (CAS) Registry Numbers for each source type is listed, where applicable. This data is provided for guidance purposes only.

13.6 Table 4 compares single laboratory accuracy and precision testing GRO in water using ERA CRM 762 proficiency sample. ERA uses 50% weathered gasoline supplied in methanol for this product. Data performed using analyzer configuration specified in Sec. 6.2., with four calibrations performed using standards prepared in hexane. Water samples were spiked in clean tap water using 40 mL VOA vials and then extracted in hexane. Sample 1 was extracted 15 minutes after preparation; Sample 2 Duplicate was extracted 1 hour after preparation. The laboratory mean result, QC and PT performance limits in ERA's proficiency study are shown for comparison. Percent recoveries (%R) in Calibration 1 and 2 are within ERA's acceptance limits. The two CRMs fluoresce differently, percent difference is 23%, due to differences in how the weathered gasolines were manufactured. Percent recovery in Calibration 3 was low, but passes the PT acceptance limit. Percent recovery in Calibration 4 was high, as expected, as fresh gasoline has fewer aromatic hydrocarbons compared to weathered gasoline. See Reference 3 in Sec. 16 for ERA 762 certificate of analysis. This data is provided for guidance purposes only.

13.7 Table 5 compares single laboratory accuracy and precision testing GRO in soil using ERA CRM 763 proficiency sample. ERA uses 50% weathered gasoline in this product, same source used in ERA CRM 762 for GRO in water. Data performed using analyzer configuration specified in Sec. 6.2., with four calibrations performed using standards prepared in methanol solvent. Sample 1 and Sample 2 Duplicate each contained 10-g of soil extracted in 20 mL methanol solvent for 24 hours. The laboratory mean result, QC and PT performance limits in ERA's proficiency study are shown for comparison. Percent recoveries (%R) in Calibration 1 and Calibration 2 are within ERA's QC and PT acceptance limits. The two CRMs fluoresce differently, percent difference is 35%, due to differences in how the weathered gasolines were manufactured. Percent recovery in Calibration 3 was low, but passes the QC and PT acceptance limits. Percent recovery in Calibration 4 was high, but it too passes the QC and PT acceptance limits. The high recovery was expected, since fresh gasoline has fewer aromatic hydrocarbons compared to weathered gasoline. See Reference 4 in Sec. 16 for ERA 763 certificate of analysis. This data is provided for guidance purposes only.

13.8 Table 6 shows single laboratory precision for GRO in soils testing blind U.S. EPA proficiency evaluation samples spiked with weathered gasoline. Data performed using analyzer configuration specified in Sec. 6.2., calibrated to Sitelab CAL-025M. Soils were analyzed on-site using 5-g samples extracted in 10 mL methanol for 2 to 3 minutes. Samples were prepared in triplicate and included unspiked samples. Split samples were analyzed by a certified laboratory using Method 8015. Relative percent difference (RPD) values between the UVF GRO and Method 8015 GRO were less than 50%. This data is a subset of analytical results performed in the U.S. EPA study in Reference 1, Table 7-9, Sec. 16, where GRO concentrations were added to DRO concentrations and reported as TPH. This data is provided for guidance purposes only.

13.9 Table 7 shows precision testing GRO in soils comparing UVF GRO results to two laboratory GC methods in samples collected from a former UST gasoline site at various concentrations. UVF data performed by single laboratory using analyzer configuration specified in Sec. 6.2., calibrated to Sitelab CAL-025M. Soils were analyzed on-site using 5-g samples extracted in 10 mL methanol for 5 to 10 minutes. Split samples were analyzed by a certified laboratory using Method 8015 for GRO and Total VPH using the MADEP VPH Method. The two methods are similar, but VPH separates hydrocarbons in the GRO range into aromatic and aliphatic fractions. BTEX compounds are also reported. See Reference 5 in Sec. 16. Results in this study show RPD values compared to both methods testing soils from low to high concentrations. Linear regression was also calculated with R-Square values >0.95. This data is provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, a free publication available from the American Chemical Society (ACS), Committee on Chemical Safety, http://portal.acs.org/portal/fileFetch/C/WPCP_012290/pdf/WPCP_012290.pdf.

15.0 WASTE MANAGEMENT

The EPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Laboratories are urged to protect air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

Field waste management procedures must also be consistent with Federal, State and local regulations.

16.0 REFERENCES

1. U.S. Environmental Protection Agency, Superfund Innovative Technology Evaluation Program, “Field Measurement Technologies for Total Petroleum Hydrocarbons in Soil,” EPA Office of Research and Development, Publication No. EPA/600/R-01/080, September 2001.

2. North Carolina Department of Environmental Quality, Division of Waste Management, Underground Storage Tank Section, “Comprehensive Tables for Corrective Action Guidelines,” September 7, 2022.

3. Environmental Resource Associates, Certified Reference Material 762, “Gasoline Range Organics (GRO) in Water,” Certificate of Analysis, Lot P321-762, February 1, 2022.

4. Environmental Resource Associates, Certified Reference Material 763, “Gasoline Range Organics (GRO) in Soil,” Certificate of Analysis, Lot D115-763, November 5, 2021.

5. Massachusetts Department of Environmental Protection, Office of Research and Standards, Bureau of Waste Site Cleanup, “Method for the Determination of Volatile Petroleum Hydrocarbons,” May 2004.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

FLUORESCENCE OF CERTIFIED REFERENCE MATERIALS USED TO ESTABLISH BASELINE CALIBRATIONS FOR GASOLINE RANGE ORGANICS (GRO) ANALYSIS

UVF Analyzer with GRO Optics, Calibrations and Analysis in Methanol Solvent		Calibration 1: Sitelab GRO Standard, (BTEX Mixture) CAL-025M		Calibration 2: 50% Weathered Gasoline, AccuStandard GA-W50-10X	
CRMs Tested at 10 ppm Concentrations	Voltage (RFU)	Response (PPM)		Response (PPM)	
Sitelab GRO Standard Response:	149	10.0		17.0	
50% Weathered Gasoline Response:	90	5.8		10.0	
Response Factor Exhibited:	1.7x	1.7x		1.7x	
Other BTEX Standards Suitable for GRO Calibration:			%D		
VPH Matrix Spike, AccuStandard GRH-004-MS-100X	147	9.9	99%	16.8	
6 Compound BTEX Mixture, AccuStandard CLP-BTEX-10X	155	10.5	105%	18.0	
Second Source Calibration Standards by Different Manufacturer:			%D		%D
6 Compound BTEX Mixture, Restek 30213	165	11.2	112%	19.2	
Unleaded Gas Standard, 50% Weathered, Restek 30098	105	6.8		12.0	120%
Response Factor Exhibited:	1.6x	1.6x		1.6x	

This data is provided for guidance purposes only. CRMs containing BTEX and weathered gasoline products made by different manufacturers were analyzed at 10 ppm and compared to Sitelab's GRO standard containing a 6 compound BTEX mixture used to establish baseline GRO measurement and AccuStandard's 50% weathered gasoline standard.

CRMs shown meet the 1.5 to 2x response factor limit and percent difference (%D) values are within the 70 to 130% acceptance range. These products qualify as second source calibration standards suitable for this method.

Raw fluorescence units (RFU) or voltage detected by the UVF is proportionate to sample concentration readings, which vary depending on which standard is used for calibration.

TABLE 2

FLUORESCENCE RESPONSE OF MONOAROMATIC HYDROCARBONS COMPARING TWO CALIBRATIONS USED TO MEASURE GASOLINE RANGE ORGANICS (GRO)

UVF Analyzer with GRO Optics, Calibrations and Analysis in Methanol Solvent	Molecular Weight ($g \cdot mol^{-1}$)	Carbon Number	Calibration 1: GRO Standard, (BTEX Mixture) Sitelab CAL-025M Fluorescence Response (%)	Calibration 2: 50% Weathered Gasoline, AccuStandard GA-W50-10X Fluorescence Response (%)
Example Compounds in C6 – C10 Range:				
Benzene	78	C6	28	48
Toluene	92	C7	114	185
Ethylbenzene	106	C8	82	140
m-Xylene	106	C8	98	165
o-Xylene	106	C8	125	210
p-Xylene	106	C8	180	330
1,2,4-Trimethylbenzene	120	C9	34	58
1,3,5-Trimethylbenzene	120	C9	140	240
Naphthalene (2-Ring PAH Compound)	128	C10	0	0
	Sitelab GRO Standard Response:		100	170
	50% Weathered Gasoline Response:		58	100

This data is provided for guidance purposes only. Fluorescence of individual compounds varies depending on the size and shape of each molecule and which standard is used for calibration. Examples shown here compare the fluorescence of monoaromatic hydrocarbons measured using Sitelab's GRO standard containing a 6 compound BTEX mixture and AccuStandard's 50% weathered gasoline standard.

TABLE 3

FLUORESCENCE RESPONSE OF GASOLINE RANGE ORGANICS IN FUELS AND OILS

UVF Analyzer with GRO Optics, Calibrations and Analysis in Methanol Solvent	CAS No.	Source	Calibration 1: GRO Standard, (BTEX Mixture) Sitelab CAL-025M Fluorescence Response (%)	Calibration 2: 50%W Gasoline, AccuStandard GA-W50-10X Fluorescence Response (%)
Automotive Fuels with Low to High GRO Content:				
Gasoline, Regular Unleaded	8006-61-9	CRM	22	36
Gasoline, Regular 87 Octane	8006-61-9	Retail	27	45
Highway Diesel, Ultra Low Sulfur	68476-34-6	Retail	30	49
No. 2 Diesel Fuel	68334-30-5	CRM	30	49
Weathered Gasoline, UST Site	N/A	NAPL	75	125
Aviation Fuels with Low to High GRO Content:				
JP-5 Jet Fuel	8008-20-6	CRM	18	29
Kerosene	8008-20-6	CRM	20	32
JET-A Jet Fuel	8008-20-6	CRM	25	40
JP-4 Jet Fuel	50815-00-4	CRM	28	44
JP-8 Jet Fuel	82863-50-1	CRM	30	48
Other Fuels and Oils with Low to High GRO Content:				
Naphtha, Oil Refinery Site	N/A	NAPL	3.2	5.0
No. 6 Fuel Oil	68553-00-4	CRM	8	14
Transformer Oil	64742-53-6	CRM	14	22
Light Crude Oil, NIST 2779	8002-05-9	SRM	15	24
No. 2 Fuel Oil	68476-30-2	CRM	25	42
Heat Transfer Fluid	101-84-8	Retail	200	320
	Sitelab GRO Standard Response:		100	170
	50% Weathered Gasoline Response:		58	100

This data is provided for guidance purposes only. Response in fuels and oils varies in GRO content, shown here calibrated to Sitelab's GRO standard containing a 6 compound BTEX mixture and AccuStandard's 50% weathered gasoline standard.

TABLE 4

GASOLINE RANGE ORGANICS IN WATER TESTING ERA 762 PROFICIENCY SAMPLE

UVF Analyzer with GRO Optics Comparing 4 Calibrations, Samples Tested in Hexane	Sample 1 µg/L	Sample 2 Duplicate µg/L	Average Result µg/L	Certified Value µg/L	%R
1. GRO Water Standard, ERA 762, Lot P321-762	2,000	2,060	2,030	2,210	92%
2. 50% Weathered Gasoline, AccuStandard GA-W50-10X	1,470	1,760	1,615	2,210	73%
3. GRO Calibration Standard, Sitelab CAL-025H	920	1,100	1,010	2,210	46%
4. Fresh Gasoline, 87 Octane, Gas Station, Massachusetts	3,500	4,180	3,840	2,210	174%
ERA Proficiency Study, Lot P321-762 Gasoline Range Organics Mean Result: (Based on 60 Lab Tests)			2,380	2,210	108%
QC Performance Acceptance Limits:			1,320 – 3,540		
PT Performance Acceptance Limits:			815 – 3,890		

This data is provided for guidance purposes only. UVF performed using four calibrations using different standards available for comparison.

Samples spiked 1:1000 in tap water using Environmental Resource Associates (ERA) 762 GRO in Water Certified Reference Material (CRM). Samples extracted using hexane. Sample 1 was extracted 15 minutes after preparation; Sample 2 was extracted 1 hour after preparation.

GRO analysis results performed best using ERA’s 762 standard and AccuStandard’s weathered gasoline calibrations. Both contain 50% weathered gasoline, but are manufactured differently. Concentrations exhibited are within ERA’s QC and PT Performance Acceptance Limits. Calibrations using Sitelab GRO and fresh, unweathered gasoline produced lower and higher recoveries due to the higher and lower aromatic composition in the standards.

TABLE 5

GASOLINE RANGE ORGANICS IN SOIL TESTING ERA 763 PROFICIENCY SAMPLE

UVF Analyzer with GRO Optics Comparing 4 Calibrations, Samples Tested in Methanol	Sample 1 mg/Kg	Sample 2 Duplicate mg/Kg	Average Result mg/Kg	Certified Value mg/Kg	%R
1. GRO Water Standard, ERA 762, Lot P321-762	450	430	440	599	73%
2. 50% Weathered Gasoline, AccuStandard GA-W50-10X	320	295	308	599	51%
3. GRO Calibration Standard, Sitelab CAL-025M	200	184	192	599	32%
4. Fresh Gasoline, 87 Octane, Gas Station, Massachusetts	760	700	730	599	122%
ERA Proficiency Study, Lot D115-763 Gasoline Range Organics Mean Result: (Based on 85 Lab Tests)			414	599	69%
QC Performance Acceptance Limits:			184 – 797		
PT Performance Acceptance Limits:			59.9 – 875		

This data is provided for guidance purposes only. UVF performed using four calibrations using different standards available for comparison.

Two soil samples containing 10 grams each were extracted in 20 mL methanol for 24 hours.

GRO analysis performed best using ERA's 762 standard and AccuStandard's weathered gasoline calibrations. Both contain 50% weathered gasoline, but are manufactured differently. Percent recovery (%R) values are within ERA's QC and PT Performance Acceptance Limits. Calibrations using Sitelab GRO and fresh, unweathered gasoline produced lower and higher recoveries due to the higher and lower aromatic composition in the standards.

TABLE 6

GASOLINE RANGE ORGANICS IN SOILS TESTING BLIND U.S. EPA PROFICIENCY EVALUATION SAMPLES SPIKED WITH WEATHERED GASOLINE

Contaminant, Matrix	U.S. EPA Sample ID Number	Certified Value mg/Kg	UVF GRO Result mg/Kg	Lab GC GRO Result mg/Kg	UVF to Lab GC RPD
Weathered Gasoline, Low Soil Samples	PE S27	0	<0.2	<0.54	0%
	PE S28	0	<0.2	<0.54	0%
	PE S29	0	<0.2	<0.54	0%
Weathered Gasoline, Medium Soil Samples	PE S30	1,090	490	575	16%
	PE S31	1,090	460	623	30%
	PE S32	1,090	560	544	3%
Weathered Gasoline, High Soil Samples	PE S63	2,780	1,660	1,400	17%
	PE S64	2,780	1,610	1,510	6%
	PE S65	2,780	1,530	1,600	4%
	PE S36	3,120	1,380	1,590	14%
	PE S37	3,120	1,530	1,760	14%
	PE S38	3,120	1,570	1,820	15%

This data is provided for guidance purposes only. Data used in EPA TPH in Soil study in Reference 1, Sec. 16.

UVF performed using configuration in Sec. 6.2., calibrated to GRO using Sitelab CAL-025M. Certified laboratory performed EPA Method 8015 to detect gasoline range organics. Data shows accuracy compared to Lab GC results testing triplicate samples spiked with low to high concentrations with weathered gasoline; relative percent difference (RPD) values were <50%.

TABLE 7

GASOLINE RANGE ORGANIC RESULTS COMPARED TO TWO LABORATORY GC METHODS TESTING SOILS FROM UNDERGROUND STORAGE TANK GASOLINE SITE

Soils with Low to High GRO Concentrations	Sample No.	UVF GRO Result mg/Kg	Lab GRO Method 8015 mg/Kg	RPD	Lab Total VPH MADEP Method mg/Kg	RPD
	1	176	260	39%	292	50%
	2	666	1,500	77%	886	28%
	3	1,481	1,500	1%	1,526	3%
	4	3,037	2,300	28%	2,665	13%
	5	5,570	8,000	36%	8,103	37%
	6	5,704	6,000	5%	7,025	21%
		Correlation Coefficient:	$R^2 = 0.9564$, $y = 0.8105x$		$R^2 = 0.9788$, $y = 0.7677x$	

Composition of VPH in Samples Reported by Lab:

Sample No.	C5-C9 Aliphatics mg/Kg	C9-C12 Aliphatics mg/Kg	C9-C10 Aromatics mg/Kg	MtBE + BTEX Compounds mg/Kg	Total VPH mg/Kg
1	45	110	130	6	292
2	140	350	380	16	886
3	99	560	730	137	1,526
4	320	1,000	1,300	45	2,665
5	1,900	2,300	2,400	1,503	8,103
6	1,900	1,700	2,500	925	7,025

This data is provided for guidance purposes only. UVF performed using configuration in Sec. 6.2., calibrated to GRO using Sitelab CAL-025M. Laboratory performed U.S. EPA Method 8015-GRO and MADEP VPH Method in split samples. Total VPH calculated as the sum of aliphatic and aromatic fractions plus target compounds. Example data shows accuracy testing contaminated soils from low to high concentrations.

FIGURE 1

2017 NORTH CAROLINA DEPARTMENT OF ENVIRONMENTAL QUALITY REGULATORY GUIDELINES USING UVF AND GAS CHROMATOGRAPHY ANALYTICAL METHODS

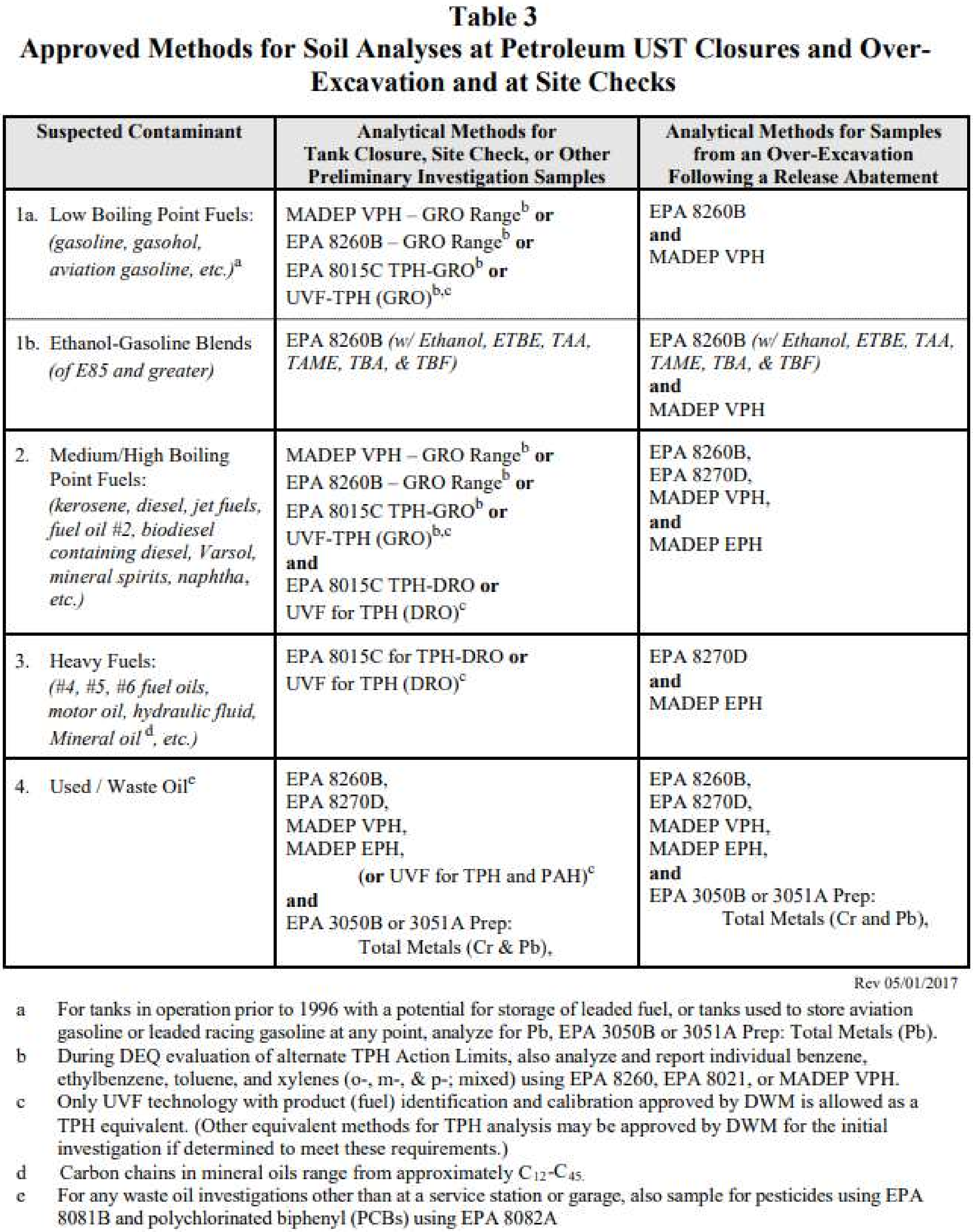

Table 3
Approved Methods for Soil Analyses at Petroleum UST Closures and Over-Excavation and at Site Checks

Suspected Contaminant	Analytical Methods for Tank Closure, Site Check, or Other Preliminary Investigation Samples	Analytical Methods for Samples from an Over-Excavation Following a Release Abatement
1a. Low Boiling Point Fuels: *(gasoline, gasohol, aviation gasoline, etc.)*[a]	MADEP VPH – GRO Range[b] **or** EPA 8260B – GRO Range[b] **or** EPA 8015C TPH-GRO[b] **or** UVF-TPH (GRO)[b,c]	EPA 8260B **and** MADEP VPH
1b. Ethanol-Gasoline Blends *(of E85 and greater)*	EPA 8260B *(w/ Ethanol, ETBE, TAA, TAME, TBA, & TBF)*	EPA 8260B *(w/ Ethanol, ETBE, TAA, TAME, TBA, & TBF)* **and** MADEP VPH
2. Medium/High Boiling Point Fuels: *(kerosene, diesel, jet fuels, fuel oil #2, biodiesel containing diesel, Varsol, mineral spirits, naphtha, etc.)*	MADEP VPH – GRO Range[b] **or** EPA 8260B – GRO Range[b] **or** EPA 8015C TPH-GRO[b] **or** UVF-TPH (GRO)[b,c] **and** EPA 8015C TPH-DRO **or** UVF for TPH (DRO)[c]	EPA 8260B, EPA 8270D, MADEP VPH, **and** MADEP EPH
3. Heavy Fuels: *(#4, #5, #6 fuel oils, motor oil, hydraulic fluid, Mineral oil*[d]*, etc.)*	EPA 8015C for TPH-DRO **or** UVF for TPH (DRO)[c]	EPA 8270D **and** MADEP EPH
4. Used / Waste Oil[e]	EPA 8260B, EPA 8270D, MADEP VPH, MADEP EPH, (**or** UVF for TPH and PAH)[c] **and** EPA 3050B or 3051A Prep: Total Metals (Cr & Pb),	EPA 8260B, EPA 8270D, MADEP VPH, MADEP EPH, **and** EPA 3050B or 3051A Prep: Total Metals (Cr and Pb),

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a For tanks in operation prior to 1996 with a potential for storage of leaded fuel, or tanks used to store aviation gasoline or leaded racing gasoline at any point, analyze for Pb, EPA 3050B or 3051A Prep: Total Metals (Pb).

b During DEQ evaluation of alternate TPH Action Limits, also analyze and report individual benzene, ethylbenzene, toluene, and xylenes (o-, m-, & p-; mixed) using EPA 8260, EPA 8021, or MADEP VPH.

c Only UVF technology with product (fuel) identification and calibration approved by DWM is allowed as a TPH equivalent. (Other equivalent methods for TPH analysis may be approved by DWM for the initial investigation if determined to meet these requirements.)

d Carbon chains in mineral oils range from approximately C_{12}-C_{45}.

e For any waste oil investigations other than at a service station or garage, also sample for pesticides using EPA 8081B and polychlorinated biphenyl (PCBs) using EPA 8082A