METHOD 8650

TOTAL PETROLEUM HYDROCARBONS, AS COMBINED GASOLINE AND DIESEL RANGE ORGANICS, 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 Total Petroleum Hydrocarbons (TPH) using Methods 8630 and 8640 to detect Gasoline Range Organics (GRO) and Diesel Range Organics (DRO) separately and adding the concentrations together to report TPH. Specifically, these methods detect monoaromatic hydrocarbons in the C6 to C10 gasoline range and polycyclic aromatic hydrocarbons in the C10 to C36 diesel and oil range.

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. In most cases, TPH contaminated samples contain many aromatic compounds which co-fluoresce with UVF instrumentation. If analyzing individual analytes is required, refer to Method 8000 or Volatile Petroleum Hydrocarbon and Extractable Petroleum Hydrocarbon (VPH/EPH) Methods using gas chromatography instrumentation for guidance.

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

1.4 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.

1.5 Choosing the appropriate calibration standards is dependent on the type or age of petroleum suspected in a sample. Results may be biased low or biased high depending on which standards are used for calibration and analysis. In general, GRO and DRO 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 and DRO 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.

1.6 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 product or refer to Method 3500 for alternative sample preparation methods.

2.2 GRO and DRO in samples can be measured using UVF instruments fitted with appropriate excitation and emission optical filters and ultraviolet light sources. Sensitivity varies depending on the types and quantities of aromatic hydrocarbons in a sample. In general, this method detects hydrocarbons in the TPH C6 – C36 carbon range.

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 Sec. 3 in Methods 8630 and 8640 for guidance.

4.0 INTERFERENCES

Refer to Sec. 4 in Methods 8630 and 8640 for guidance.

5.0 SAFETY

Refer to Sec. 5 in Methods 8630 and 8640 for guidance.

6.0 EQUIPMENT AND SUPPLIES

Refer to Sec. 6 in Methods 8630 and 8640 for guidance.

7.0 REAGENTS AND STANDARDS

Refer to Sec. 7 in Methods 8630 and 8640 for guidance.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Refer to Sec. 8 in Methods 8630 and 8640 for guidance.

9.0 QUALITY CONTROL

Refer to Sec. 9 in Methods 8630 and 8640 for guidance.

10.0 CALIBRATION AND STANDARDIZATION

Refer to Sec. 10 in Methods 8630 and 8640 for guidance.

11.0 PROCEDURE

Refer to Sec. 11 in Methods 8630 and 8640 for guidance.

12.0 DATA ANALYSIS AND CALCULATIONS

Add the concentrations of GRO and DRO in sample results to report TPH concentration. Refer to Sec. 12 in Methods 8630 and 8640 for guidance.

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. <u>Performance data must not be used as absolute QC acceptance criteria for laboratory QC or accreditation</u>.

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 Tables 1 and 2 show the fluorescence response of aromatic hydrocarbons using different calibration standards to measure GRO and DRO content in TPH. These tables are referenced and described further in Methods 8630 and 8640. Data performed by a single laboratory testing individual compounds using AccuStandard Certified Reference Materials (CRMs) supplied in methanol. 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. Fluorescence also varies depending on which standard is used for GRO and DRO calibrations. This data is provided for guidance purposes only.

13.4 Table 3 shows the fluorescence response of GRO and DRO content in a variety of fuels and oils. Data performed by a single laboratory with analyzer configurations specified in Sec. 6.0 in Methods 8630 and 8640, calibrated using standards specified in Sec. 7.0 in Methods 8630 and 8640 used to establish baseline GRO and DRO measurement. Fluorescence response was calculated by dividing each sample's result by the concentration tested and shown as a percentage. 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 for comparison. NAPLs, heavy fuels and oils were supplied in hexane with standards prepared in methanol for analysis. Gasolines, aviation fuels and diesels 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.

13.5 Table 4 shows single laboratory accuracy testing TPH in water, as combined GRO and DRO, using two lots of Environmental Resource Associates (ERA) CRM 794 proficiency samples. These CRMs contain weathered gasoline and diesel mixtures at different concentrations. Data performed with analyzer configurations specified in Sec. 6.0 in Methods 8630 and 8640, calibrated using standards prepared in hexane. Water samples were spiked 1000:1 in clean tap water using 40 mL VOA vials and then extracted in hexane 1 hour after preparation. The laboratory mean result, QC and PT performance limits in ERA's proficiency studies are shown for comparison. Percent recoveries (%R) performed with ERA's 794 TPH in water standards using the fuel concentrations listed in each lot to calibrate for GRO and DRO were close to 100%. Percent recoveries using AccuStandard's weathered gasoline and No. 2 diesel fuel standards to calibrate for GRO and DRO were 66% and 68%. Percent recoveries using Sitelab's GRO and EDRO standards were lower at 41% and 43%, but pass ERA's acceptance limits. Low TPH recoveries were due to the DRO calibrations, as expected, since ERA uses ultra-low sulfur diesel fuel in their product which contains fewer aromatic hydrocarbons compared to AccuStandard's No. 2 diesel fuel and Sitelab's EDRO standard. See Reference 3 and 4 in Sec. 16 for ERA 794 certificates of analysis. This data is provided for guidance purposes only.

13.5 Table 5 shows single laboratory accuracy testing TPH in soil, as combined GRO and DRO, using ERA CRM 796 and 797 proficiency samples. These CRMs contain weathered gasoline and diesel mixtures at low and high concentrations. Data performed with analyzer configurations specified in Sec. 6.0 in Methods 8630 and 8640, calibrated using standards prepared in methanol. Samples were prepared using 10-g of soil extracted in 20 mL methanol for 24 hours. The laboratory mean result, QC and PT performance limits in ERA's proficiency studies are shown for comparison. Percent recoveries (%R) using AccuStandard's weathered gasoline and No. 2 diesel fuel standards to calibrate for GRO and DRO were 79% and 58% and pass ERA's QC and PT acceptance limits. Percent recoveries using Sitelab's GRO and EDRO standards were lower at 51% and 38%, but pass ERA's PT acceptance limits. Recoveries were low due to the DRO content in the soil. In this case, ERA used a high composition (93%) of ultra-low sulfur diesel fuel to prepare CRM 797. This fuel type fluoresces weaker in the DRO range and stronger in the GRO range. ERA used a lower composition (48%) of diesel to prepare CRM 796 and TPH recoveries were more favorable. See Reference 5 and 6 in Sec. 16 for ERA certificates of analysis. This data is provided for guidance purposes only.

13.6 Table 6 shows TPH results in soils compared to TPH results performed by a certified laboratory using the Massachusetts Dept. of Environmental Protection (MADEP) VPH/EPH Methods testing soils contaminated with jet fuel from a U.S. Air Force Base. Data performed by a single laboratory with analyzer configurations specified in Sec. 6.0 in Methods 8630 and 8640, calibrated to Sitelab's GRO and EDRO standards in methanol. Soils were analyzed on-site using 5-g each extracted in 10 mL methanol. Split samples having low to high concentrations were sent to the laboratory for confirmation analysis. Total VPH and Total EPH was calculated as the sum of the aliphatic and aromatic fractions plus target analytes detected in each method. Despite the poor correlation testing the GRO and EDRO concentrations, good correlation was exhibited for TPH concentrations with relative percent difference (RPD) values <50% compared to the lab's TPH results. Jet fuels are made with kerosene and contain high compositions of aliphatic hydrocarbons which do not fluoresce. Additionally, aromatic hydrocarbons that do exist are abundant near the C10 to C12 carbon range, the cutoff point where the GRO/EDRO and VPH/EPH test methods can overlap. See Reference 7 and 8 in Sec. 16 for further guidance.

13.7 Table 7 shows spike recovery testing gasoline range and diesel range organics in water using JP-5 jet fuel laboratory control samples. Data performed by a single laboratory with analyzer configurations specified in Sec. 6.0 in Methods 8630 and 8640, calibrated to Sitelab's GRO and EDRO standards in hexane. Samples were spiked in clean tap water using 40 mL VOA vials at three concentrations using AccuStandard CRM p/n FU-012-40X supplied in methanol, same source used to prepare 10, 20 and 40 ppm LCS standards in hexane for analysis to compare fluorescence response. Samples 1 were extracted in hexane 10 minutes after preparation; Samples 2 were extracted in hexane 1 hour after preparation. TPH was reported as average sum of GRO and EDRO concentrations. Percent recoveries (%R) exhibited were >80% compared to the LCS standards. In this case, JP-5 jet fuel fluoresces 5.5 times lower measured for GRO and 25 times lower measured for EDRO due to the low composition of aromatic hydrocarbons in the fuel. This data is provided for guidance purposes only.

13.8 Table 8 shows single laboratory accuracy and precision performed in U.S. EPA TPH in soil study testing blind proficiency evaluation soils and liquid neat samples. UVF analysis performed using configurations specified in Sec. 6.0 in Methods 8630 and 8640, testing samples for GRO and EDRO content using methanol. Split samples were analyzed by a certified laboratory using Method 8015M. TPH reported as sum of GRO and EDRO concentrations performed by both UVF and Lab GC methods. Samples were prepared in triplicate and spiked with weathered gasoline and No. 2 diesel fuel. UVF TPH results correlated well to the Lab GC TPH results and are within most of the acceptance limits. See Reference 1 in Sec. 16 for U.S. EPA's study. This data is provided for guidance purposes only.

13.9 Tables 9 and 10 show single laboratory accuracy and precision performed in U.S. EPA TPH in soil study testing blind proficiency evaluation soils containing weathered gasoline and No. 2 diesel fuel with spiked additives and interferences. UVF analysis performed using configurations specified in Sec. 6.0 in Methods 8630 and 8640, testing samples for GRO and EDRO content using methanol. TPH reported as the combined GRO and EDRO concentrations. UVF TPH results in Tables 9 and 10 were lower compared to the certified values, but were within the acceptance limits without spiked additives. See Reference 1 in Sec. 16 for U.S. EPA's study. This data is provided for guidance purposes only.

13.10 Table 11 shows single laboratory accuracy performed by Cranfield University in the United Kingdom for the European Fuel Manufacturers Association's Conservation of Clean Air and Water in Europe (Concawe), comparing UVF results to laboratory GC/MS results in soils spiked with gasoline and diesel fuel. UVF analysis performed using a multi-wavelength scanning fluorometer with similar configurations specified in Sec. 6.0 in Methods 8630 and 8640, testing samples for GRO and DRO content using methanol extraction. TPH reported as the combined GRO and DRO concentrations. Relative percent difference (RPD) values for GRO, DRO and TPH were <20%. See Reference 9 in Sec. 16 for Concawe's study. 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 794, “Texas Low-Level Fuels (TPH) in Water,” Certificate of Analysis, Lot P315-794, June 29, 2021.

4. Environmental Resource Associates, Certified Reference Material 794, “Texas Low-Level Fuels (TPH) in Water,” Certificate of Analysis, Lot P321-794, February 1, 2022.

5. Environmental Resource Associates, Certified Reference Material 796, “Texas Low-Level Fuels (TPH) in Soil,” Certificate of Analysis, Lot D115-796, December 1, 2021.

6. Environmental Resource Associates, Certified Reference Material 797, “Texas High-Level Fuels (TPH) in Soil,” Certificate of Analysis, Lot D116-797, February 3, 2022.

7. 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.

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

9. F. Coulon, P. Campo, C. Walton, M.C. Alamar, T. Cowley, N. Marsay and I. Tezyapar, “Qualitative and Quantitative Comparison of Field-Based Technologies for Petroleum Hydrocarbons Determination in Soils,” Conservation of Clean Air and Water in Europe (Concawe), Report No. 12/22, Brussels, July 2022.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

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

TABLE 1

FLUORESCENCE RESPONSE OF AROMATIC HYDROCARBONS COMPARING TWO CALIBRATIONS USED TO MEASURE GASOLINE RANGE ORGANIC CONTENT IN TPH

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 2

FLUORESCENCE RESPONSE OF AROMATIC HYDROCARBONS COMPARING TWO CALIBRATIONS USED TO MEASURE DIESEL RANGE ORGANIC CONTENT IN TPH

UVF Analyzer with DRO Optics, Calibrations and Analysis in Methanol Solvent	Molecular Weight ($g \cdot mol^{-1}$)	Carbon Number	Calibration 1: No. 2 Diesel Fuel, AccuStandard FU-009-40X Fluorescence Response (%)	Calibration 2: Sitelab EDRO, (50%W Diesel) CAL-042M Fluorescence Response (%)
Polycyclic Aromatic Compounds:				
Naphthalene	128	C10	134	84
2-Methylnaphthalene	142	C11	260	160
Phenanthrene	178	C14	1,460	900
Anthracene	178	C14	2,080	1,280
Benzo[a]Anthracene	228	C18	212	130
Chrysene	228	C18	1,200	740
Benzo[k]Fluoranthene	252	C20	376	230
Benzo[a]Pyrene	252	C20	200	122
Dibenz[a,h]Anthracene	278	C22	20	12
Sitelab EDRO Standard Response:			162	100
No. 2 Diesel Fuel Standard Response:			100	62
Monoaromatic Compounds:				
Benzene	78	C6	0.16	0.10
Toluene	92	C7	0.40	0.25
Ethylbenzene	106	C8	0.32	0.20
m-Xylene	106	C8	0.54	0.34
o-Xylene	106	C8	0.80	0.50
p-Xylene	106	C8	1.60	1.00
1,3,5-Trimethylbenzene	120	C9	2.30	1.50

This data is provided for guidance purposes only. Analytes provided in methanol using CRMs by AccuStandard. Fluorescence of individual compounds varies depending on the size and shape of each molecule and which standard is used for calibration. PAH compounds in the C10 – C20 range exhibit high response. Monoaromatic compounds in the C6 – C10 range exhibit very low response and contribute little to DRO detection in this method.

TABLE 3

FLUORESCENCE RESPONSE COMPARING GRO AND DRO CONTENT IN FUEL AND OILS

UVF with GRO and DRO Optics, Calibrations and Analysis in Methanol Solvent	Source	CAS No.	GRO 8630: BTEX Mixture Fluorescence Response (%)	DRO 8640: No.2 Diesel Fuel Fluorescence Response (%)
GRO and DRO Content in Gasolines and Aviation Fuels:				
Gasoline, Regular 87 Octane	Retail	8006-61-9	27	1.2
50% Weathered Gasoline	CRM	8006-61-9	58	10
Weathered Gasoline, UST Site	NAPL	N/A	75	16
Kerosene	CRM	8008-20-6	20	2.9
JP-5 Jet Fuel	CRM	8008-20-6	18	7.2
JET-A Jet Fuel	CRM	8008-20-6	25	8.0
GRO and DRO Content in Diesel Fuels and Heating Oils:				
Ultra-Low Sulfur Diesel Fuel	CRM	68476-34-6	29	12
Highway Diesel, Ultra-Low Sulfur	Retail	68476-34-6	30	29
50% Weathered Diesel	CRM	68334-30-5	23	162
Weathered Diesel, UST Site	NAPL	N/A	20	145
No. 2 Fuel Oil	CRM	68476-30-2	25	110
No. 4 Fuel Oil	CRM	68476-31-3	16	256
No. 6 Fuel Oil	CRM	68553-00-4	8	427
GRO and DRO Content in Other Oils:				
Vacuum Pump Oil	Retail	64741-88-4	1.1	2.7
Transformer Oil	CRM	64742-53-6	14	16
Light Crude Oil, NIST 2779	SRM	8002-05-9	15	122
	GRO Standard Response for Comparison:		100	
	DRO Standard Response for Comparison:			100

This data is provided for guidance purposes only. UVF performed using calibration standards specified in Methods 8630 and 8640 for baseline GRO and DRO measurement.

TABLE 4

TOTAL PETROLEUM HYDROCARBONS IN WATER, AS COMBINED GASOLINE AND DIESEL RANGE ORGANICS, TESTING TWO LOTS OF ERA CRM 794 PROFICIENCY SAMPLES

UVF Calibrations and Sample Analysis in Hexane Solvent	GRO Result mg/L	DRO Result mg/L	TPH Result mg/L	Certified TPH Value mg/L	%R
Lot 1 Water Study:					
1. TPH Water Standard, ERA 794, Lot P315-794	3.10	3.00	6.10	6.21	98%
2. AccuStandard Standards, Weathered Gas and Diesel	3.50	0.58	4.08	6.21	66%
3. Sitelab Standards, GRO and EDRO	2.20	0.36	2.56	6.21	41%
ERA TPH in Water Proficiency Study Mean Result (Based on 1 Lab Test):			5.52	6.21	89%
QC Performance Acceptance Limits:			1.58 – 9.07		
PT Performance Acceptance Limits:			0 – 10.9		
Lot 2 Water Study:					
1. TPH Water Standard, ERA 794, Lot P321-794	2.54	2.80	5.34	5.45	98%
2. AccuStandard Standards, Weathered Gas and Diesel	3.18	0.54	3.72	5.45	68%
3. Sitelab Standards, GRO and EDRO	2.00	0.34	2.34	5.45	43%
ERA TPH in Water Proficiency Study Mean Result (Based on 2 Lab Tests):			3.86	5.45	71%
QC Performance Acceptance Limits:			1.38 – 7.96		
PT Performance Acceptance Limits:			0 – 9.6		

This data is provided for guidance purposes only. Environmental Resource Associates (ERA) 794 contains variable mixtures of 50% weathered gasoline and ultra-low sulfur diesel used to validate the Texas TX-1005 Method.

Calibrations 1 performed with ERA 794 CRMs using the fuel concentrations in each lot for GRO and DRO calibration:
TPH composition in ERA 794 Lot 1 contains 3.5 mg/L weathered gasoline and 2.71 mg/L diesel fuel.
TPH composition in ERA 794 Lot 2 contains 2.66 mg/L weathered gasoline and 2.79 mg/L diesel fuel.

Calibrations 2 performed using AccuStandard's 50% weathered gasoline standard, p/n GA-W50-10X for GRO analysis and No. 2 diesel fuel, p/n FU-009-40X for DRO analysis.

Calibrations 3 performed using Sitelab's GRO standard, p/n CAL-025H for GRO analysis and EDRO standard, p/n CAL-042H for DRO analysis.

TABLE 5

TOTAL PETROLEUM HYDROCARBONS IN SOIL, AS COMBINED GASOLINE AND DIESEL RANGE ORGANICS, TESTING ERA CRM 796 AND 797 PROFICIENCY SAMPLES

UVF Calibrations and Sample Analysis in Methanol Solvent	GRO Result mg/Kg	DRO Result mg/Kg	TPH Result mg/Kg	Certified TPH Value mg/Kg	%R
Texas Low-Level Fuels (TPH) in Soil: ERA 796, Lot D115-796					
1. AccuStandard Standards, Weathered Gas and Diesel	23	27	50	63.3	79%
2. Sitelab Standards, GRO and EDRO	15	17	32	63.3	51%
ERA TPH in Soil Proficiency Study Mean Result (Based on 4 Lab Tests):			82.3	63.3	130%
QC Performance Acceptance Limits:			26.0 – 91.8		
PT Performance Acceptance Limits:			9.5 – 108		
Texas High-Level Fuels (TPH) in Soil: ERA 797, Lot D116-797					
1. AccuStandard Standards, Weathered Gas and Diesel	3,300	1,200	4,500	7,760	58%
2. Sitelab Standards, GRO and EDRO	2,200	750	2,950	7,760	38%
ERA TPH in Soil Proficiency Study Mean Result (Based on 4 Lab Tests):			9,300	7,760	120%
QC Performance Acceptance Limits:			4,200 – 10,200		
PT Performance Acceptance Limits:			2,690 – 11,800		

This data is provided for guidance purposes only. Environmental Resource Associates (ERA) 796 and 797 contain variable mixtures of 50% weathered gasoline and ultra-low sulfur diesel used to validate the Texas TX-1005 Method.

Calibrations 1 performed using AccuStandard's 50% weathered gasoline standard, p/n GA-W50-10X for GRO analysis and No. 2 diesel fuel, p/n FU-009-40X for DRO analysis.

Calibrations 2 performed using Sitelab's GRO standard, p/n CAL-025M for GRO analysis and EDRO standard, p/n CAL-042M for DRO analysis.

TPH composition in ERA 796 contains 32.6 mg/Kg weathered gasoline and 30.7 mg/Kg diesel fuel.
TPH composition in ERA 797 contains 565 mg/Kg weathered gasoline and 7,190 mg/Kg diesel fuel.

TABLE 6

TOTAL PETROLEUM HYDROCARBONS IN SOILS, AS COMBINDED GRO AND EDRO, FROM U.S. AIR FORCE BASE JET FUEL SITE COMPARED TO MADEP VPH/EPH METHOD

Concentrations in mg/Kg	UVF GRO	Lab GC Total VPH	UVF EDRO	Lab GC Total EPH	UVF TPH	Lab GC TPH	RPD
Soil 1	6.0	8.0	1.0	ND <0.4	7.0	8.0	15%
Soil 2	4,760	1,100	680	4,400	5,440	5,500	1%
Soil 3	6,270	4,200	700	5,000	6,970	9,200	28%
Soil 4	7,797	6,500	950	6,700	8,747	13,200	41%
Soil 5	9,763	3,900	1,175	7,000	10,938	10,900	0.4%
Soil 6	16,380	6,000	1,800	12,000	18,180	18,000	1%
				Correlation Coefficient:	R^2 = 0.972; y = 0.8962x		

This data is provided for guidance purposes only. UVF performed using configurations in Sec. 6.2.1 and 6.2.2, calibrated to Sitelab's GRO and EDRO standards testing soils with methanol. UVF TPH reported as sum of GRO and EDRO concentrations. Laboratory used MADEP VPH/EPH GC Method; TPH reported as the sum of Total VPH and Total EPH concentrations testing split samples. Example data shows TPH accuracy testing contaminated soils from low to high concentrations.

TABLE 7

SPIKE RECOVERY TESTING GASOLINE RANGE AND DIESEL RANGE ORGANICS IN WATER USING JP-5 JET FUEL LABORATORY CONTROL SAMPLES

UVF Calibrations and Analysis in Hexane	Samples 1 10 Minutes mg/L	Samples 2 1 Hour mg/L	Average Result mg/L	JP-5 Jet Fuel LCS Standard Response mg/L	%R
Water Samples with 10 mg/L JP-5 Jet Fuel:					
GRO Calibration, Sitelab CAL-025H	1.44	1.60	1.52	1.80	84%
EDRO Calibration, Sitelab CAL-042H	0.35	0.37	0.36	0.40	90%
	Total Petroleum Hydrocarbons:		1.87	2.22	84%
Water Samples with 20 mg/L JP-5 Jet Fuel:					
GRO Calibration, Sitelab CAL-025H	3.20	3.40	3.30	3.60	92%
EDRO Calibration, Sitelab CAL-042H	0.76	0.80	0.78	0.80	98%
	Total Petroleum Hydrocarbons:		4.08	4.40	93%
Water Samples with 40 mg/L JP-5 Jet Fuel:					
GRO Calibration, Sitelab CAL-025H	7.10	7.12	7.11	7.20	99%
EDRO Calibration, Sitelab CAL-042H	1.61	1.59	1.60	1.60	100%
	Total Petroleum Hydrocarbons:		8.71	8.80	99%

This data is provided for guidance purposes only. UVF performed using configurations in Sec. 6.2.1 and 6.2.2, calibrated to Sitelab's GRO and EDRO standards. Samples extracted and analyzed 10 minutes and 1 hour after preparation to check aqueous stability. Total Petroleum Hydrocarbons reported as average sum of GRO and DRO concentrations. Percent recoveries (%R) exhibited were >50% compared to the LCS standard responses.

TABLE 8

TOTAL PETROLEUM HYDROCARBONS, AS COMBINED GRO AND EDRO, TESTING BLIND U.S. EPA PROFICIENCY EVALUATION SOILS AND LIQUID NEAT SAMPLES

Contaminant, Matrix	U.S. EPA Sample ID Number	Certified Value mg/Kg	UVF TPH Result mg/Kg	Lab GC TPH Result mg/Kg	Acceptance Limits mg/Kg
Weathered Gasoline, Low Soil Samples	PE S27	0	1.1	5.12	0 – 2
	PE S28	0	1.1	13.1	0 – 2
	PE S29	0	2.1	13.5	0 – 2
Weathered Gasoline, Medium Soil Samples	PE S30	1,090	520	702	389 – 1,548
	PE S31	1,090	490	743	389 – 1,548
	PE S32	1,090	590	671	389 – 1,548
Weathered Gasoline, High Soil Samples	PE S63	2,780	1,660	1,740	992 – 3,950
	PE S64	2,780	1,610	1,980	992 – 3,950
	PE S65	2,780	1,530	2,050	992 – 3,950
	PE S36	3,120	1,450	1,880	1,110 – 4,430
	PE S37	3,120	1,600	2,020	1,110 – 4,430
	PE S38	3,120	1,650	2,180	1,110 – 4,430
No. 2 Diesel Fuel, Low Soil Samples (For MDL Study)	PE S66	37.3	17.9	12.0	18.1 – 47.4
	PE S67	37.3	18.9	16.5	18.1 – 47.4
	PE S68	37.3	17.5	13.7	18.1 – 47.4
	PE S69	37.3	15.8	16.4	18.1 – 47.4
	PE S70	37.3	18.1	17.4	18.1 – 47.4
	PE S71	37.3	19.0	17.2	18.1 – 47.4
	PE S72	37.3	18.5	14.8	18.1 – 47.4
No. 2 Diesel Fuel, Medium Soil Samples	PE S80	454	290	226	220 – 577
	PE S81	454	300	265	220 – 577
	PE S82	454	300	267	220 – 577
No. 2 Diesel Fuel, High Soil Samples	PE S86	3,920	2,800	2,480	1,900 – 4,980
	PE S87	3,920	3,050	2,890	1,900 – 4,980
	PE S88	3,920	2,600	2,800	1,900 – 4,980
	PE S101	4,320	2,870	2,700	2,100 – 5,490
	PE S102	4,320	3,340	2,950	2,100 – 5,490
	PE S103	4,320	3,100	3,070	2,100 – 5,490
Weathered Gasoline, Liquid Neat Samples	PE L119	814,100	606,770	656,000	N/A
	PE L120	814,100	574,880	611,000	N/A
	PE L121	814,100	576,200	677,000	N/A
No. 2 Diesel Fuel, Liquid Neat Samples	PE L116	851,900	719,800	1,090,000	N/A
	PE L117	851,900	762,200	1,020,000	N/A
	PE L118	851,900	737,400	1,160,000	N/A

This data is provided for guidance purposes only. Data source: U.S. EPA Publication EPA/600/R-01/080.

TABLE 9

TOTAL PETROLEUM HYDROCARBONS, AS COMBINED GRO AND EDRO, TESTING BLIND U.S. EPA PROFICIENCY EVALUATION WEATHERED GASOLINE SOILS WITH SPIKED ADDITIVES AND INTERFERENCES

Contaminant, with Spike Added	U.S. EPA Sample ID Number	Certified Value mg/Kg	UVF TPH Result mg/Kg	Acceptance Limits without Spiked Additives mg/Kg
Weathered Gasoline with 1,100 ppm MtBE	PE S39	2,830	1,320	1,010 – 4,020
	PE S40	2,830	1,370	1,010 – 4,020
	PE S41	2,830	1,560	1,010 – 4,020
Weathered Gasoline with 1,760 ppm MtBE	PE S42	2,490	890	889 – 3,540
	PE S43	2,490	1,030	889 – 3,540
	PE S44	2,490	1,030	889 – 3,540
Weathered Gasoline with 2,900 ppm Stoddard Solvent	PE S51	2,770	1,580	989 – 3,930
	PE S52	2,770	1,580	989 – 3,930
	PE S53	2,770	1,490	989 – 3,930
Weathered Gasoline with 15,400 ppm Stoddard Solvent	PE S54	2,730	1,650	970 – 3,880
	PE S55	2,730	2,490	970 – 3,880
	PE S56	2,730	2,010	970 – 3,880
Weathered Gasoline with 2,810 ppm Tetrachloroethylene	PE S45	3,030	1,660	1,080 – 4,300
	PE S46	3,030	1,910	1,080 – 4,300
	PE S47	3,030	1,500	1,080 – 4,300
Weathered Gasoline with 13,100 ppm Tetrachloroethylene	PE S48	2,800	1,300	1,000 – 3,980
	PE S49	2,800	1,380	1,000 – 3,980
	PE S50	2,800	1,490	1,000 – 3,980
Weathered Gasoline with 2,730 ppm Turpentine	PE S57	2,950	1,530	1,050 – 4,190
	PE S58	2,950	1,410	1,050 – 4,190
	PE S59	2,950	1,240	1,050 – 4,190
Weathered Gasoline with 12,900 ppm Turpentine	PE S60	2,950	1,530	1,050 – 4,190
	PE S61	2,950	1,410	1,050 – 4,190
	PE S62	2,950	1,240	1,050 – 4,190

This data is provided for guidance purposes only. Data source: U.S. EPA Publication EPA/600/R-01/080.

TABLE 10

TOTAL PETROLEUM HYDROCARBONS, AS COMBINED GRO AND EDRO, TESTING BLIND U.S. EPA PROFICIENCY EVALUATION DIESEL FUEL SOILS WITH SPIKED ADDITIVES AND INTERFERENCES

Soil Contaminant with Spike Added	U.S. EPA Sample ID Number	Certified Value mg/Kg	UVF TPH Result mg/Kg	Acceptance Limits without Spiked Additives mg/Kg
No. 2 Diesel Fuel	PE S01	3,920	2,860	1,900 – 4,980
with 3,650 ppm	PE S02	3,920	3,080	1,900 – 4,980
Stoddard Solvent	PE S03	3,920	2,830	1,900 – 4,980
No. 2 Diesel Fuel	PE S04	3,920	2,830	1,900 – 4,980
with 18,200 ppm	PE S05	3,920	2,510	1,900 – 4,980
Stoddard Solvent	PE S06	3,920	2,570	1,900 – 4,980
No. 2 Diesel Fuel	PE S07	3,920	2,830	1,900 – 4,980
with 3,850 ppm	PE S08	3,920	2,840	1,900 – 4,980
Turpentine	PE S09	3,920	2,720	1,900 – 4,980
No. 2 Diesel Fuel	PE S10	3,920	2,270	1,900 – 4,980
with 19,600 ppm	PE S11	3,920	2,250	1,900 – 4,980
Turpentine	PE S12	3,920	2,150	1,900 – 4,980
No. 2 Diesel Fuel	PE S89	3,920	2,590	1,900 – 4,980
with 3,350 ppm	PE S90	3,920	2,690	1,900 – 4,980
1,2,4-Trichlorobenzene	PE S91	3,920	2,660	1,900 – 4,980
No. 2 Diesel Fuel	PE S92	3,920	2,420	1,900 – 4,980
with 16,600 ppm	PE S93	3,920	2,300	1,900 – 4,980
1,2,4-Trichlorobenzene	PE S94	3,920	2,400	1,900 – 4,980
No. 2 Diesel Fuel	PE S95	3,920	2,430	1,900 – 4,980
with 3,940 ppm	PE S96	3,920	2,750	1,900 – 4,980
Humic Acid	PE S97	3,920	2,860	1,900 – 4,980
No. 2 Diesel Fuel	PE S98	3,920	2,560	1,900 – 4,980
with 19,500 ppm	PE S99	3,920	2,430	1,900 – 4,980
Humic Acid	PE S101	3,920	2,480	1,900 – 4,980
Humic Acid Only	PE S104	0	11	N/A
3,940 ppm	PE S105	0	12	N/A
	PE S106	0	13	N/A
Humic Acid Only	PE S107	0	45	N/A
19,500 ppm	PE S108	0	35	N/A
	PE S109	0	32	N/A

This data is provided for guidance purposes only. Data source: U.S. EPA Publication EPA/600/R-01/080.

TABLE 11

CONCAWE PERFORMANCE STUDY TESTING TPH, AS COMBINED GRO AND DRO, IN SPIKED SOIL SAMPLES USING A MULTI-WAVELENGTH SCANNING FLUOROMETER

	Spike Conc. mg/Kg	Lab RT GRO mg/Kg	UVF GRO RPD	Lab RT DRO mg/Kg	UVF DRO RPD	Lab RT TPH mg/Kg	UVF TPH RPD
Gasoline Spiked Soil Samples							
Silty Loam Clay	100	47	6%	43	6%	90	7%
	1,000	692	14%	173	13%	865	14%
	10,000	8,245	3%	292	17%	8,537	4%
Clay Loam	100	54	13%	33	7%	87	6%
	1,000	717	8%	101	4%	818	8%
	10,000	8,298	9%	313	6%	8,611	8%
Sandy Loam	100	23	2%	67	6%	90	5%
	1,000	543	7%	211	11%	754	2%
	10,000	7,409	2%	1,004	10%	8,413	1%
Diesel Fuel Spiked Soil Samples							
Silty Loam Clay	100	16	14%	63	1%	79	2%
	1,000	250	2%	583	4%	833	2%
	10,000	2,495	8%	6,107	8%	8,602	8%
Clay Loam	100	17	2%	69	9%	86	8%
	1,000	292	13%	542	7%	834	9%
	10,000	1,633	13%	6,533	10%	8,166	10%
Sandy Loam	100	8	5%	78	6%	86	4%
	1,000	237	15%	587	19%	824	9%
	10,000	2,343	19%	5,736	2%	8,079	4%

This data is provided for guidance purposes only. Data source: Concawe Report No. 12/22 using Tables 8 and 9.

UVF analysis performed using QED HC-1 analyzer and proprietary calibration standards manufactured by QROS, Ltd, configured with similar UV light and optics specified in Methods 8630 and 8640 using fixed-wavelength fluorometers. Lab RT (Reference Technology) performed using U.S. EPA Methods 5021 and 8260 by GC/MS. Sample results in GRO detected in C5-C9 range and DRO detected in C10-C40 range, were rounded to whole numbers and added together to report TPH in C5-C40 range. Relative percent difference (RPD) values, reported as %Diff in the tables, were <20%.

Samples were prepared using three soil types spiked with gasoline (CAS No. 86290-81-5) and high-sulfur diesel fuel (CAS No. 68334-30-5) collected from a local petrol station in the United Kingdom. All samples were tested in triplicate; the mean results were reported.

Concawe is a division of the European Fuel Manufacturers Association.

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