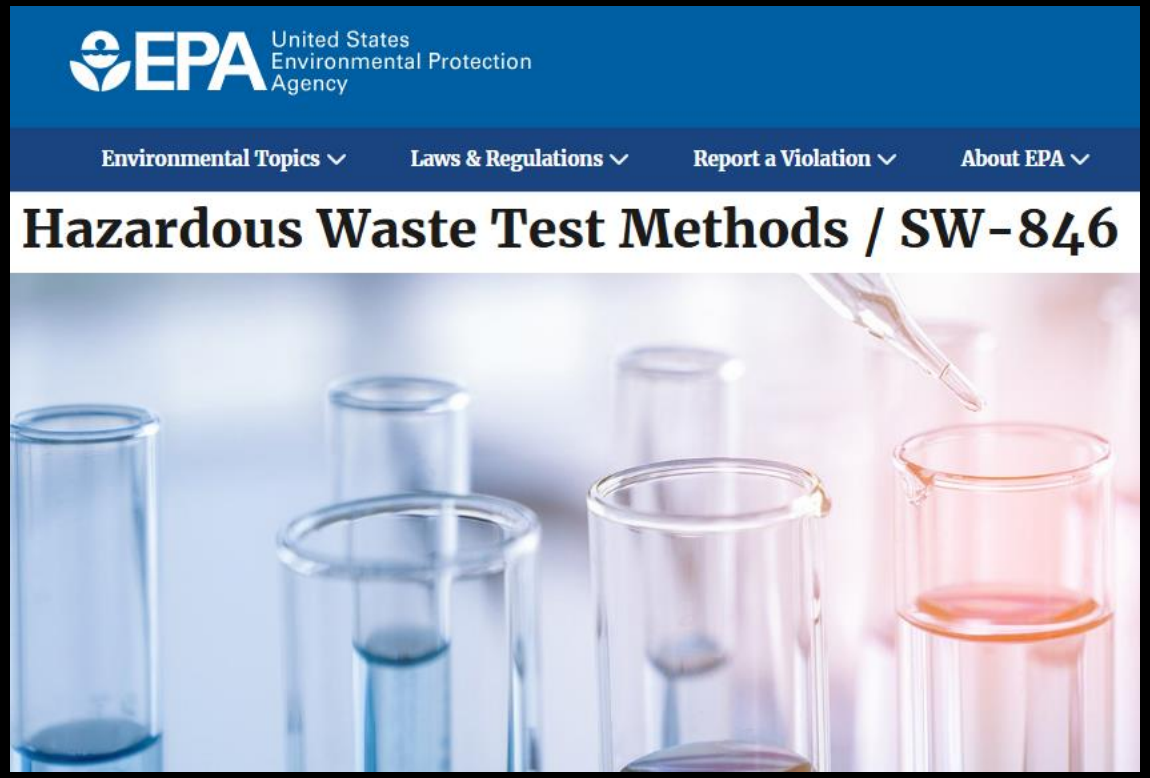
New Hydrocarbon Test Methods Submitted to U.S. EPA SW-846 Program

Presented By: Steve Greason
Sitelab Corporation
West Newbury, Massachusetts

Approved Organic Test Methods



Source: https://www.epa.gov/hw-sw846

Method No. 8000 Series	Method Type Organic Determinative Methods
80xx	GC Determinative/Various Detectors
81xx	GC Determinative/Various Detectors
82xx	GC Determinative/Mass Spec Detectors
83xx	HPLC Determinative/Various Detectors
832x	HPLC Determinative/Mass Spec Detectors
84xx	IR Determinative
85xx	UV/Vis Determinative

New Ultraviolet Fluorescence (UVF) Test Methods

In 2024, five new methods for measuring hydrocarbons using UVF instrumentation submitted for approval in U.S. EPA's SW-846 Compendium.

The methods provide quick, low cost, quantitative results and detect a wide range of petroleum contaminants in soil or water using solvent extraction.

Ideal for on-site screening analysis!

8000 Series: Organic Determinative Methods	
86xx	UVF Determinative – New Category!
8630	Gasoline Range Organics (GRO)
8640	Diesel Range Organics (DRO)
8650	Total Petroleum Hydrocarbons (TPH, GRO+DRO)
8660	Total Petroleum Hydrocarbons (TPH, source oil)
8670	Polycyclic Aromatic Hydrocarbons (PAHs)

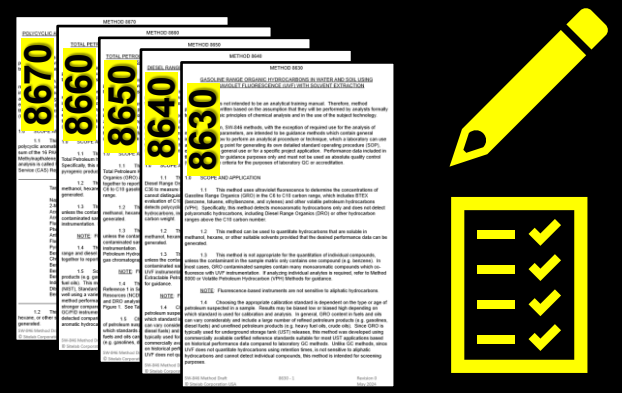
Methods Created using U.S. EPA SW-846 Style Guide

The format and boilerplate descriptions used were taken from these guidelines for consistency with other methods.

Method performance tables were developed to meet EPA's Validation and Peer Review of U.S. Environmental Protection Agency Chemical Methods of Analysis.

Includes general fluorescence of hydrocarbons within each method, proficiency sample analysis and correlation to other determinative methods.

Methods were peer reviewed and edited by two industry experts…



Dr. Nancy Rothman: New Horizons Environmental, Inc.

Jerry Parr: Catalyst Information Resources, LLC

Sitelab Corporation

First started using fluorometers in 1995

Analyzers manufactured for Sitelab by Turner Designs, Inc. (San Jose, CA)

Products and services include:

- Instrument sales and rentals
- Sample test kits and supplies
- Calibration kits
- Laboratory analysis and consulting

EPA Evaluation Study in 2001
Publication No. EPA/600/R-01/080

“Field Measurement Technologies for Total Petroleum Hydrocarbons in Soil”

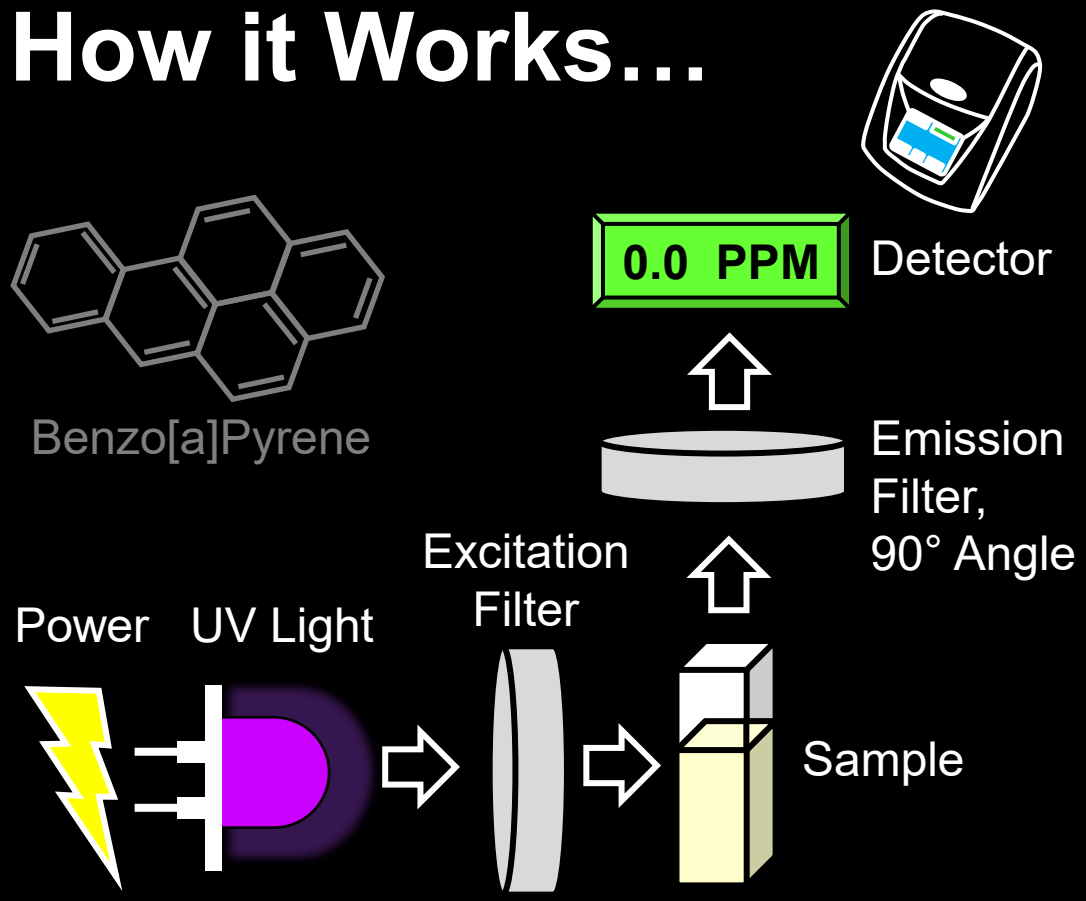
Types of UVF Analyzers

1. Fixed-wavelength fluorometers
2. Continuous flow, on-line fluorometers
3. Multi-wavelength scanning fluorometers
4. Laser induced fluorescence (LIF)

UVF is sensitive to aromatic hydrocarbons only. Aliphatics do not fluoresce!

UVF cannot detect individual compounds

How it Works…



Detector converts voltage to concentration

Instrument Configurations using Sitelab UVF-Trilogy

Method	Module	Excitation	Emission	Hydrocarbons Detected
8630	GRO	254 nm	270-290 nm	C6-C10 Range
8640	EDRO	254 nm	300-400 nm	C10-C36 Range
8670	PAHS	254 nm	400-420 nm	C12-C22 Range
8660	TPH OIL	365 nm	420-600 nm	C14-C50 Range

Fluorescence modules are fitted with LED UV lights and optical filters

Other, similar configurations exist and can be used, specified in each method

Extraction Solvents Specified for Sample Analysis

Use HPLC grade solvents only!

Soils, sediments, most other solid samples

Use methanol, methyl alcohol or other polar solvents

Fresh water, salt water, ground-water, other aqueous samples

Use hexane, n-hexane or other non-polar solvents

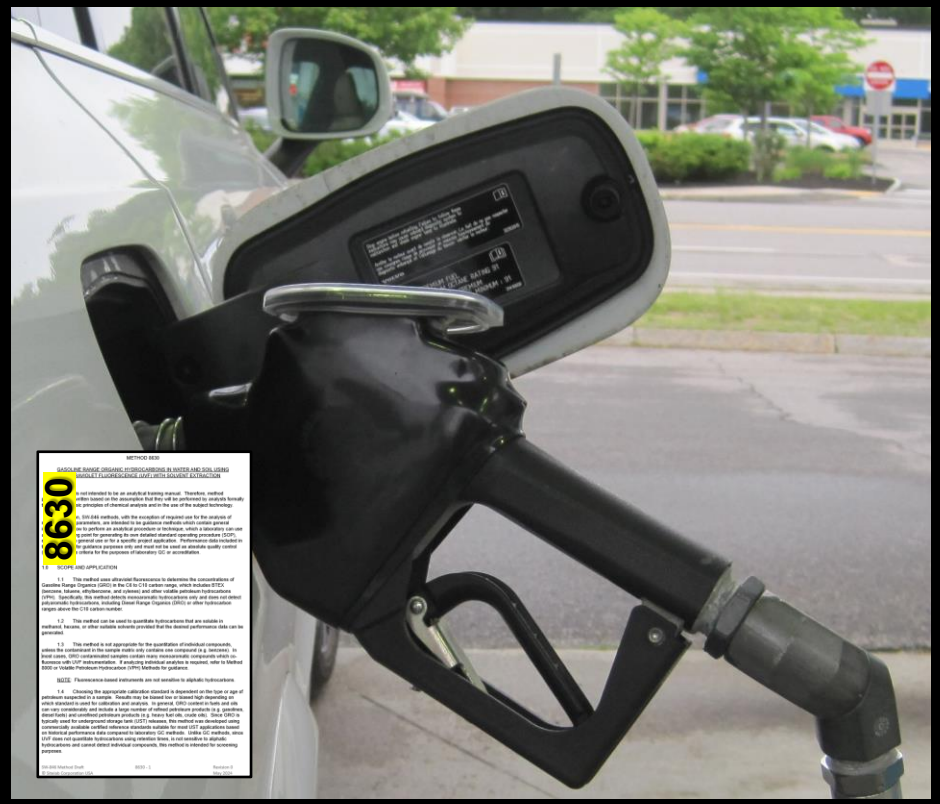
Oils, fuels, Non-Aqueous Phase Liquids (NAPL), sludges or wastes

Use hexane, or use methanol if appropriate

Methanol
CAS No.
67-56-1

Hexane
CAS No.
110-54-3

Method 8630: Gasoline Range Organics



8630 has 7 Method Performance Tables

Common Applications:

Gasolines, jet fuels

Diesel fuels, home heating oils

Gas condensates

Other, light-refined petroleum products

Detects GRO in TPH Method 8650

UVF-Trilogy with GRO UV Module

Analyzer detects volatile petroleum hydrocarbons in C6 to C10 range

Method 8630 correlates best to EPA Method 8015 or Total VPH by GC

GRO Response Testing Monoaromatic Compounds

Hydrocarbons Tested using 2 Calibrations:	BTEX Mixture Response (%)	Weathered Gasoline Response (%)
Benzene, C6	28	48
Toluene, C7	114	185
Ethylbenzene, C8	82	140
m-Xylene, C8	98	165
o-Xylene, C8	125	210
p-Xylene, C8	180	330
1,3,5-Trimethylbenzene, C9	140	240

Fluorescence varies due to size and shape of each molecule and which standard is used to calibrate

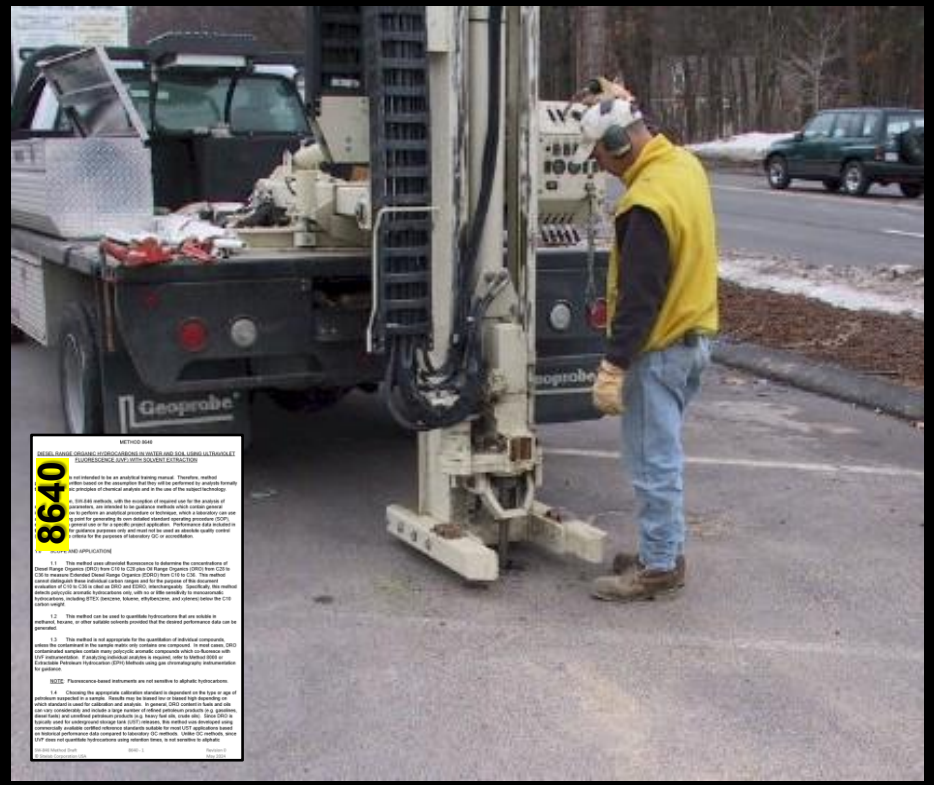
Sitelab GRO calibration kit in methanol or hexane contains a BTEX mixture

Method 8630: GRO Proficiency Study Samples

ERA 763 GRO in Soil Comparing 3 Calibrations	Certified Value mg/Kg	UVF Result mg/Kg	Recovery %	PT Performance Acceptance Limits mg/Kg	
Sitelab GRO Standard	599	192	32%	59.9 – 875	ERA study mean result = 414 ppm (85 lab tests)
50% Weathered Gasoline Standard	599	308	51%	59.9 – 875	
ERA 762 GRO Standard	599	440	73%	59.9 – 875	

EPA 2001 TPH Soil Study using Sitelab GRO Standard		Certified Value mg/Kg	UVF Result mg/Kg	vs. Lab GC Result mg/Kg	UVF to Lab GC RPD	
PE S29	Low Soil Sample	0	<0.2	<0.54	0%	Soils made with 50% weathered gasoline
PE S32	Medium Soil Sampe	1,090	560	544	3%	
PE S38	High Soil Sample	3,120	1,570	1,820	15%	

Method 8640: Diesel Range Organics



8640 has 11 Method Performance Tables

Common Applications:

Diesels, heating oils

Gasolines, jet fuels

Crude oils, lube oils, transformer oils

Refined petroleum products

Detects DRO in TPH Method 8650

UVF-Trilogy with EDRO UV Module

Analyzer detects diesel and oil range organics in C10 to C36 range

Method 8640 correlates best to EPA Method 8015M or Total EPH by GC

DRO Response Testing Polyaromatic Compounds

Hydrocarbons Tested using 2 Calibrations:	Weathered Diesel Response (%)	No. 2 Diesel Fuel Response (%)
Naphthalene, C10	84	134
2-Methylnapthalene, C11	160	260
Phenanthrene, C14	900	1,460
Anthracene, C14	1,280	2,080
Benzo[k]Fluoranthene, C20	230	376
Benzo[a]Pyrene, C20	122	200
Dibenz[a,h]Anthracene, C22	12	20

Fluorescence varies due to size and shape of each molecule and which standard is used to calibrate

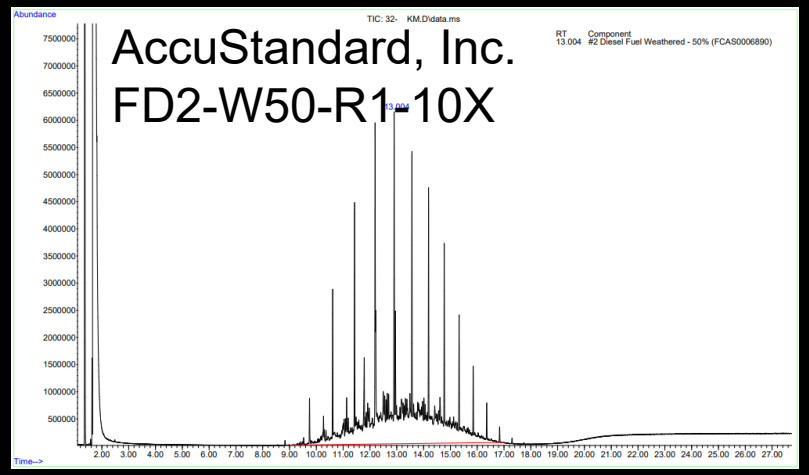
Sitelab EDRO calibration kit in methanol or hexane contains weathered diesel

Method 8640: DRO Proficiency Study Samples

ERA 765 DRO in Soil Comparing 3 Calibrations	Certified Value mg/Kg	UVF Result mg/Kg	Recovery %	PT Performance Acceptance Limits mg/Kg	
Sitelab EDRO Standard	1,850	195	11%	478 – 2,220	Soil made with ultra-low sulfur diesel fuel
No. 2 Diesel Fuel Standard	1,850	315	17%	478 – 2,220	
ERA 764 DRO Standard	1,850	1,860	101%	478 – 2,220	

EPA 2001 TPH Soil Study Sitelab EDRO Calibration		Certified Value mg/Kg	UVF Result mg/Kg	vs. Lab GC Result mg/Kg	EPA Acceptance Limits mg/Kg	
PE S66	7 Spiked samples used for MDL study	37.3	17.9	12.0	18.1 – 47.4	Soils made with traditional high sulfur diesel fuel
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	UVF MDL = 3.4
PE S71		37.3	19.0	17.2	18.1 – 47.4	Lab MDL = 6.32
PE S72		37.3	18.5	14.8	18.1 – 47.4	

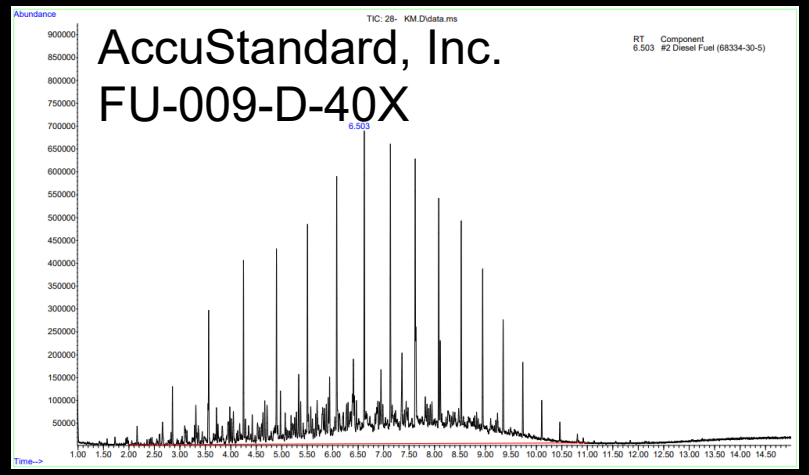
Chromatograms Comparing Diesel Fuel CRMs



50% Weathered Diesel Fuel
CAS# 68334-30-5

Contains high sulfur

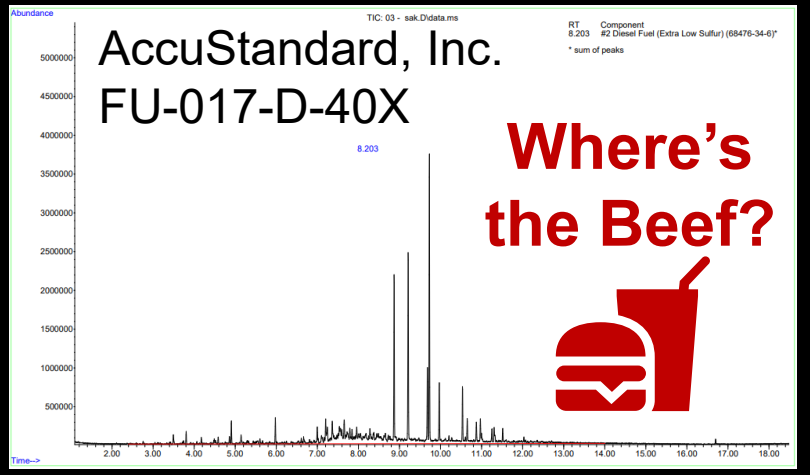
Used in Sitelab EDRO, fluoresces stronger due to more aromatics



Traditional No. 2 Diesel Fuel
CAS# 68334-30-5

Contains high sulfur

Fluoresces slightly weaker, used for Method 8640 baseline measurement



Clean Burning, Highway Diesel
CAS# 68476-34-6 ← Different CAS

Contains ultra or extra low sulfur

Fluoresces much weaker, contains fewer aromatics and not much else!

Method 8650: TPH as GRO + DRO Fractions

Method is used to report Total Petroleum Hydrocarbons (TPH) in C6 to C36 range

Uses Methods 8630 and 8640

Gasoline and diesel range results are added together to calculate TPH concentration

Used where laboratory GC analysis using GRO/DRO or VPH/EPH methods are required

8650 has 11 Method Performance Tables

Method 8650: GRO & DRO Content in Fuels & Oils

Fluorescence Response Testing
Samples at 100 ppm

	Source	GRO 8630 BTEX Mixture Response (%)	DRO 8640 No. 2 Diesel Fuel Response (%)
1. Gasoline, Regular 87 Octane	Retail	27	1.2
2. 50% Weathered Gasoline	CRM	58	10
3. Weathered Gasoline, UST Site	NAPL	75	16
4. JET-A Jet Fuel	CRM	25	8
5. Transformer Oil	CRM	14	16
6. Highway Diesel, Ultra-Low Sulfur	Retail	30	29
7. No. 2 Fuel Oil	CRM	25	110
8. Weathered Diesel, UST Site	NAPL	20	145
9. Light Crude Oil, NIST 2779	SRM	15	122
10. No. 6 Fuel Oil	CRM	8	427

Example data from Table 3

Gasolines and aviation fuels exhibit higher GRO response

Heating oils and crudes oils exhibit higher DRO response

UVF Approved by North Carolina DEQ for UST Sites

8650 Figure 1 has NC DEQ Approved Methods

State approved use of UVF methods in Underground Storage Tank (UST) cleanup regulations in 2017. Same as Method 8650

Used in UST trust fund reimbursement program

In most cases, UVF can be used instead of GC-FID methods to report TPH as GRO+DRO

Sitelab's analyzers and the QED analyzer by QROS (UK), are used everywhere in the State

Method 8660: TPH using Source Oil to Calibrate

Method is used to measure Total Petroleum Hydrocarbon (TPH) content in water or soil

This method is site-specific. Analyzer is calibrated using the oil or fuel from a site

Mostly used in oil and gas production or refining where the oil is readily available

Different optical configurations can be used, sensitive to the hydrocarbons of interest

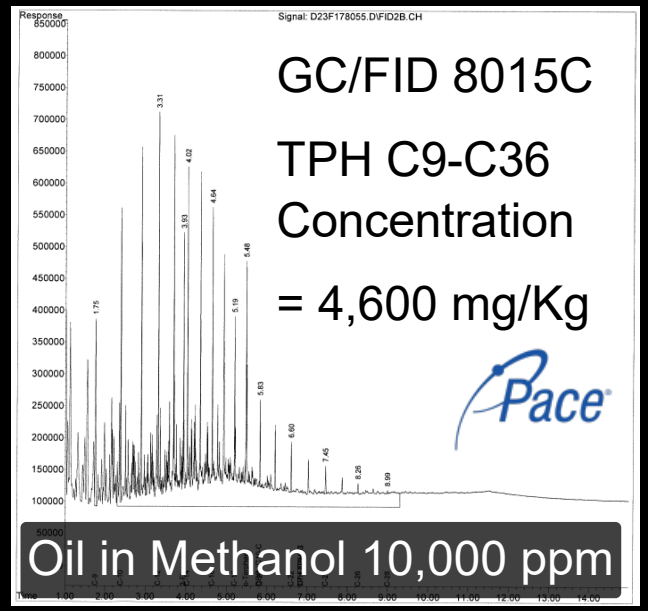
8660 has 6 Method Performance Tables

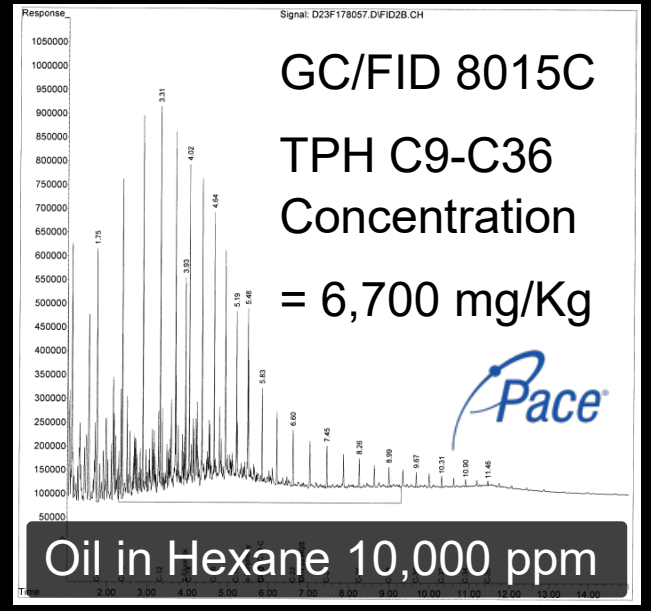
Method 8660 Developed using NIST 2779 Crude Oil

Oil extracted in methanol and hexane for 24 hours

Hexane dissolves all the oil into solution, including asphaltenes, methanol does not

Methanol extract dissolves well, is stable in water





NIST SRM 2779 is abundant with PAHs!

Very suitable to validate TPH Method 8660

Fluorescence Response Comparing 3 UVF Analyzers

NIST 2779 Crude Oil Calibrations and Analysis in Methanol Solvent	UVF-Trilogy DRO Optics 255-nm LED Response (%)	UVF-Trilogy TPHOIL Optics 365-nm LED Response (%)	UVF-500D Channel A Optics 375-nm LED Response (%)
Highway Diesel, Low Sulfur	24	0.6	0.5
No. 2 Diesel Fuel, High Sulfur	83	2.8	2.1
No. 2 Fuel Oil	90	3.5	3.4
No. 4 Fuel Oil	206	200	200
No. 6 Fuel Oil	350	420	440
Lighter Crude Oil	42	45	48
Heavier Crude Oil	224	275	280
vs. NIST Oil Standard Response	100	100	100

UVF-Trilogy with TPHOIL Module

UVF-500D fitted with same optics

Spike Recovery Analysis Testing Crude Oil in Water

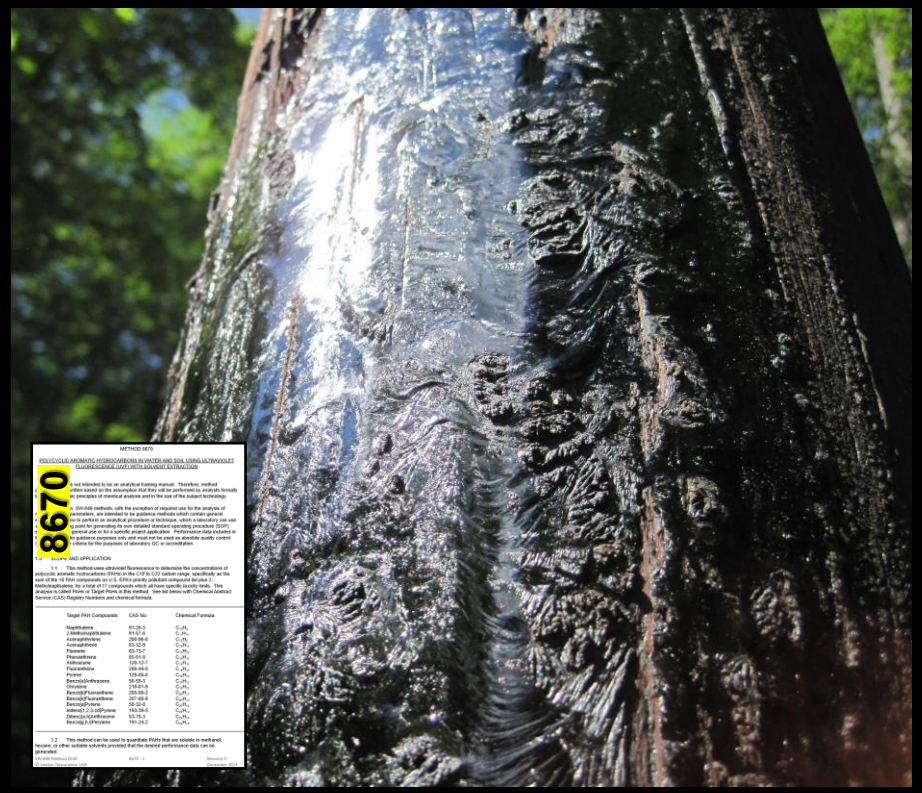
NIST 2779 Crude Oil Calibrations, Samples Extracted in Hexane Same Day and 10 Days After Preparation		10 ppm Spiked Samples Fresh Water %Recovery	10 ppm Spiked Samples Salt Water %Recovery	20 ppm Spiked Samples Fresh Water %Recovery	20 ppm Spiked Samples Salt Water %Recovery
UVF-Trilogy, 255-nm LED using DRO Optics	30 Minutes	101%	95%	88%	89%
	10 Days Old	86%	93%	82%	84%
UVF-Trilogy, 365-nm LED using TPHOIL Optics	30 Minutes	100%	94%	92%	95%
	10 Days Old	80%	86%	82%	81%
UVF-500D, 375-nm LED using Channel A Optics	30 Minutes	94%	90%	86%	89%
	10 Days Old	78%	81%	80%	77%

Aqueous Stability Testing Spiked Water Over Time

NIST 2779 Crude Oil Calibrations, Samples Tested Without Hexane Extraction		No Spike mg/L	5 Minutes mg/L	24 Hours mg/L	5 Days mg/L	10 Days mg/L	%Drop in Conc.
UVF-Trilogy, 255-nm LED	Salt Water 10 ppm	0.0	4.4	3.9	3.7	3.4	23%
using DRO Optics	Fresh Water 10 ppm	0.0	5.9	4.4	3.6	3.4	42%
UVF-Trilogy, 365-nm LED	Salt Water 10 ppm	1.8	17.5	15.0	14.0	12.4	29%
using TPHOIL Optics	Fresh Water 10 ppm	0.7	15.9	15.1	8.1	6.2	61%
UVF-500D, 375-nm LED	Salt Water 10 ppm	2.6	16.8	14.1	13.5	12.4	26%
using Channel A Optics	Fresh Water 10 ppm	1.6	14.5	14.2	8.1	6.0	59%

Data from Table 6. Study conducted to mimic continuous flow, oil-in-water monitors

Method 8670: Polycyclic Aromatic Hydrocarbons



8670 has 10 Method Performance Tables

Common Applications:

Coal tars, coal ash

Creosotes

Fuel oils, waste oils

Reclaimed asphalts

Sealcoating products

Other contaminants high in PAH content

UVF-Trilogy with PAHS UV Module

Analyzer detects Target PAHs as the sum of EPA's regulated compounds

Method 8670 correlates best to EPA Methods 8270, 8310 or 8100

Fluorescence Response Testing PAH Compounds

Hydrocarbons Tested Comparing 2 Calibrations	Molecular Weight	17 PAH Mixture Response (%)	16 PAH Mixture Response (%)	RPD
2-Methylnaphthalene, C11	142	0.20	0.18	10.5%
Phenanthrene, C14	178	12	11	8.0%
Anthracene, C14	178	475	440	7.6%
Fluoranthene, C16	202	13	12	6.6%
Pyrene, C16	202	14	13	7.5%
Benzo[a]Anthracene, C18	228	94	87	7.7%
Benzo[k]Fluoranthene, C20	252	645	600	7.2%
Benzo[a]Pyrene, C20	252	330	308	6.9%
17 Compound Standard Response:		100	93	7.3%
16 Compound Standard Response:		108	100	7.7%

Sitelab PAH calibration kit in methanol or hexane contains 17 compounds

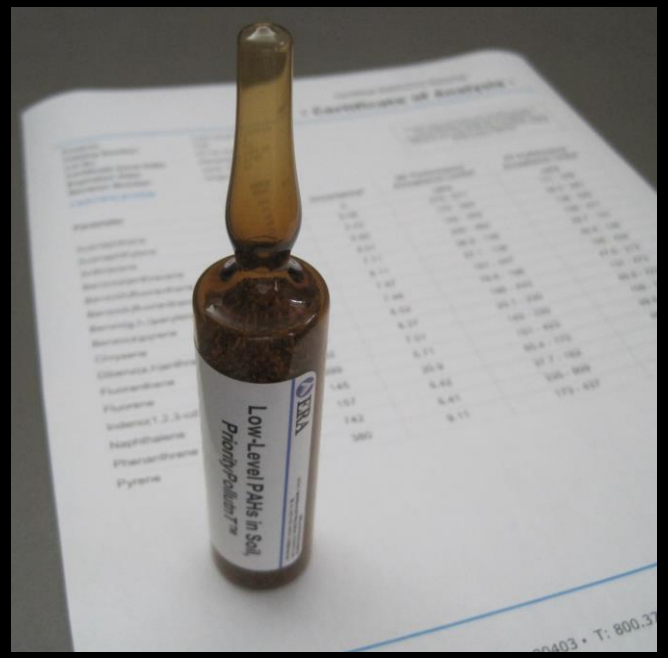
AccuStandard CRMs used:

DRH-006S: 17 Compounds

ASM-098-5X: 16 Compounds

Performance Testing PAH Proficiency Samples

Results in ppb ERA 722 PAHs in Soil	Test Result	Total 16 PAHs	Recovery %
Sitelab PAHs CAL-060M	4,700	5,838	81%
vs. ERA Study Mean	4,029	5,838	69%
ERA 715 PAHs in Water			
Sitelab PAHs CAL-060H	51.0	70.5	72%
ERA PAH Water Standard	71.0	70.5	101%
vs. ERA Study Mean	57.4	70.5	81%



ERA's 722 and 715 products contain 16 PAH compounds which vary from lot to lot

Spike Recovery Analysis using 17 Compound Mixture

Samples Tested in Methanol UVF Calibrated to PAHs using Sitelab CAL-060M	No Spike mg/Kg	Sample with 5 ppm Spike mg/Kg	Recovery	Sample with 200 ppm Spike mg/Kg	Recovery
Playground Sand	0.02	5.2	104%	202	101%
Sandy Loam Soil	0.06	4.8	95%	184	92%
Clay	0.04	4.6	91%	180	90%
ERA 570 TPH Soil	1.6	6.2	92%	182	90%
Charcoal Grill Briquets	11	13	40%	82	36%
Charcoal Grill Ash	0.08	0.12	0.8%	3.8	1.9%

Additional PAH Method for Testing EPH Aromatics?

Samples Tested in Methanol UVF Calibrated to PAHs using Sitelab CAL-060M	Sample Number	UVF EPH Aromatics mg/Kg	Lab MADEP EPH C11-C22 Aromatics mg/Kg	RPD
Tank Farm, Massachusetts	1	1,100	1,130	3%
Mixed Fuel Oil Site	2	3,585	4,600	25%
	3	7,200	6,820	5%
Wire Factory, Connecticut	4	5,250	4,800	9%
No. 6 Fuel Oil Site	5	9,100	11,000	19%
	6	23,600	21,000	12%

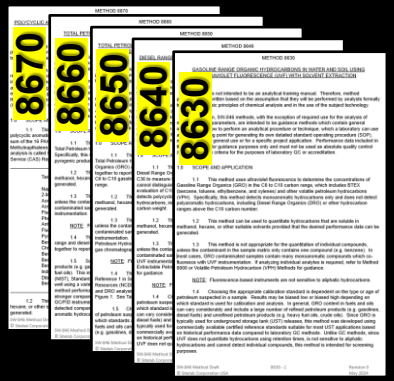
Method 8670 Table 10 Data

EPH is detected using DRO Optics

Project Took 2 Years to Complete… And Lots of $$$

Progress with EPA Has Been Slow…

Maybe Approval Will Happen in 2025?



Visit site-lab.com website for updates

The End, Thank You

Contact Info: Steve Greason
Sitelab Corporation
Website: www.site-lab.com
Phone: 978-363-2299
Email: sgreason@site-lab.com