



Sitelab’s UVF analyzers use ultraviolet fluorescence to determine the concentrations of Total Petroleum hydrocarbons (TPH) using the source oil or fuel for calibration and analysis. Specifically, this method detects aromatic hydrocarbons in oils, fuels and other petrogenic or pyrogenic products. UVF is not sensitive to aliphatic hydrocarbons.

Source oils vary considerably and include a large number of refined petroleum products (e.g. gasolines, diesel fuels) and unrefined petroleum products (e.g. crude oils, heavy fuel oils). This method was developed using National Institute of Standards & Technology (NIST), Standard Reference Material (SRM) 2779 Gulf of Mexico crude oil. This oil fluoresces well using a variety of different UV lights, optical configurations and solvents. This product is useful to validate UV fluorescence-based technologies. Oil extracted in hexane fluoresces stronger compared to the oil extracted in methanol. Oil extracts analyzed by a laboratory using GC/FID instrumentation in Figures 1 and 2 show chromatograms and hydrocarbon content detected comparing the two solvents.

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Table 1	Fluorescence Response of Aromatic Hydrocarbons, Fuels and Oils Comparing Three UVF Analyzers Calibrated to Light Crude Oil
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Figure 2	Chromatogram of 10,000 ppm NIST SRM 2779 Oil Extract in Methanol



TABLE 1

FLUORESCENCE RESPONSE OF AROMATIC HYDROCARBONS, FUELS AND OILS  
COMPARING THREE UVF ANALYZERS CALIBRATED TO LIGHT CRUDE OIL

NIST SRM 2779 Crude Oil Calibrations and Analysis in Methanol Solvent		UVF-Trilogy: 255-nm UV, EDRO Optics	UVF-Trilogy: 365-nm UV, TPHOIL Optics	UVF-500D, 375-nm UV, Channel A Optics
	CAS No.	Fluorescence Response (%)	Fluorescence Response (%)	Fluorescence Response (%)
Aromatic Compounds and Carbon Size:				
Benzene, C6	71-43-2	0.1	0.0	0.0
m-Xylene, C8	108-38-3	0.3	0.0	0.0
Naphthalene, C10	91-20-3	112	0.1	0.1
Phenanthrene, C14	85-01-8	1,200	11	13
Anthracene, C14	120-12-7	1,730	1,700	2,000
Benzo[a]Anthracene, C18	56-55-3	172	350	120
Chrysene, C18	218-01-9	970	4.8	3.0
Benzo[a]Pyrene, C20	50-32-8	160	13,000	12,500
Dibenz[a,h]Anthracene, C22	53-70-3	15	55	47
Automotive Fuels, Heating Oils and Crude Oils:				
Gasoline, Regular 87 Octane	8006-61-9	1.0	0.1	0.1
Highway Diesel, Ultra Low Sulfur	68476-34-6	24	0.6	0.5
No. 2 Diesel Fuel	68334-30-5	83	2.8	2.1
No. 2 Fuel Oil	68476-30-2	90	3.5	3.4
No. 4 Fuel Oil	68476-31-3	206	200	200
No. 6 Fuel Oil	68553-00-4	350	420	440
Crude Oil, API Gravity 40°	8002-05-9	42	45	48
Crude Oil, API Gravity 32°	8002-05-9	224	275	280
Crude Oil, API Gravity 20°	8002-05-9	97	125	130
NIST SRM 2779 Oil Calibration Standard Response:		100	100	100

This data is provided for guidance purposes only. UVF performed by Sitalab Corporation comparing three UVF analyzers fitted with different ultraviolet light sources and optical filters. Crude oil calibrations performed using NIST SRM 2779 extracted in hexane with standards prepared in methanol. Fluorescence varies depending on the size and shape of aromatic molecules and composition of hydrocarbons in different petroleum products.

TABLE 2

FLUORESCENCE OF LIGHT CRUDE OIL EXTRACTS AND STANDARDS USING HEXANE  
AND METHANOL SOLVENTS COMPARED TO UVF TPH FACTORY CALIBRATIONS

		UVF-Trilogy, 365-nm UV with TPHOIL Optics:		
NIST SRM 2779 Crude Oil Extracts, Solvent Used	Standard Concentration, Solvent Used	Voltage, Raw Fluorescence Units (RFU)	Calibration 1, Sitelab CAL-057H mg/L	Calibration 2, Sitelab CAL-057M mg/Kg
10,000 ppm Oil Extract in Hexane Solvent	10 ppm Hexane Standard	14,600	18.8	21.0
	10 ppm Methanol Standard	13,170	16.9	18.6
	RPD:	10%	11%	12%
10,000 ppm Oil Extract in Methanol Solvent	10 ppm Hexane Standard	5,280	7.0	7.8
	10 ppm Methanol Standard	6,640	8.9	9.9
	RPD:	23%	24%	23%
Factory Calibration Standard and Solvent Blank Response:				
Sitelab CAL-057H	10 ppm Hexane Standard	7,550	10.0	11.0
Sitelab CAL-057M	10 ppm Methanol Standard	6,780	9.0	10.0
	RPD:	11%	11%	10%
	Hexane Solvent Blank	80	0.0	0.0
	Methanol Solvent Blank	90	0.0	0.0

This data is provided for guidance purposes only. UVF performed by Sitelab Corporation using analyzer sensitive to crude oils. Oil standards made from NIST SRM 2779 Gulf of Mexico light crude oil and were measured to two factory calibrations using standards in hexane and methanol made from a different source of hydrocarbons.

Raw Fluorescence Units (RFU) response is voltage detected by the analyzer with or without calibration and is proportionate to sample concentration readings; relative percent difference (RPD) values are similar.

Fluorescence varies depending on which solvents are used to extract the oil and prepare standards for analysis. Oils were extracted for 24 hours using methanol and hexane. The solvents exhibit different extraction efficiency. Methanol does not extract asphaltenes in the oil; they do not dissolve and stick inside the glass extraction vial. Hexane dissolves all the asphaltene content into solution.

TABLE 3

**SPIKE RECOVERY ANALYSIS COMPARING THREE UVF ANALYZERS  
TESTING CLEAN SOILS SPIKED WITH NIST SRM 2779 CRUDE OIL**

Analyzers Calibrated to NIST 2779, Samples Tested in Duplicate	Sample with No Spike mg/Kg	Low Spike 100 ppm mg/Kg	%R	High Spike 5,000 ppm mg/Kg	%R
<b>1. UVF-Trilogy, 255-nm UV with EDRO Optics:</b>					
Beach Sand 1	0.7	96	95%	4,420	88%
Beach Sand 2	0.6	95	94%	4,560	91%
Sandy Loam 1	1.1	92	91%	4,130	83%
Sandy Loam 2	1.1	92	91%	4,540	91%
Clay 1	0.5	84	84%	4,000	80%
Clay 2	0.4	87	87%	4,530	91%
<b>2. UVF-Trilogy, 365-nm UV with TPOIL Optics:</b>					
Beach Sand 1	3.2	87	83%	3,400	68%
Beach Sand 2	2.8	88	85%	3,710	74%
Sandy Loam 1	6.0	58	52%	2,700	54%
Sandy Loam 2	6.3	65	59%	3,510	70%
Clay 1	0.6	32	32%	2,500	50%
Clay 2	0.7	35	34%	3,370	67%
<b>3. UVF-500D, 375-nm UV with Channel A Optics:</b>					
Beach Sand 1	14.6	105	90%	3,520	70%
Beach Sand 2	16.4	113	96%	3,765	75%
Sandy Loam 1	9.2	66	57%	2,800	56%
Sandy Loam 2	9.6	74	65%	3,230	64%
Clay 1	1.2	35	34%	2,600	52%
Clay 2	1.0	38	37%	3,155	63%

This data is provided for guidance purposes only. UVF performed by Sitelab Corporation using three analyzers fitted with different ultraviolet light sources and optical filters calibrated to NIST SRM 2779 using crude oil extracted in hexane with standards prepared in methanol.

Samples 1 and 2 prepared using 10-g and 5-g aliquots extracted in 20 mL methanol solvent for 24 hours. Low Spikes prepared using a 10,000 ppm oil extract dissolved in hexane. High Spikes prepared using the oil. Percent recovery (%R) values account for concentrations in samples with no spike added.

TABLE 4

**SPIKE RECOVERY ANALYSIS COMPARING THREE UVF ANALYZERS  
TESTING CONTAMINATED SOILS SPIKED WITH NIST SRM 2779 CRUDE OIL**

UVF Analyzers and Calibrations Performed	ERA 570 TPH in Soil CRMs	Sample with No Spike mg/Kg	Sample with Spike mg/Kg	Oil Spike Concentration mg/Kg	%R
<b>1. UVF-Trilogy, 255-nm UV with EDRO Optics:</b>					
Crude Oil Calibration, NIST SRM 2779	Soil Lot 1	76	3,900	5,000	76%
	Soil Lot 2	45	4,590	5,000	91%
Factory Calibration, CAL-042M	Soil Lot 1	57	3,000	5,000	59%
	Soil Lot 2	33	3,510	5,000	70%
<b>2. UVF-Trilogy, 365-nm UV with TPHOIL Optics:</b>					
Crude Oil Calibration, NIST SRM 2779	Soil Lot 1	121	2,500	5,000	48%
	Soil Lot 2	120	3,100	5,000	60%
Factory Calibration, CAL-057M	Soil Lot 1	236	4,850	5,000	92%
	Soil Lot 2	233	5,780	5,000	116%
<b>3. UVF-500D, 375-nm UV with Channel A Optics:</b>					
Crude Oil Calibration, NIST SRM 2779	Soil Lot 1	152	2,560	5,000	48%
	Soil Lot 2	175	3,325	5,000	63%
Factory Calibration, CAL-056M-500D	Soil Lot 1	308	5,120	5,000	96%
	Soil Lot 2	350	6,650	5,000	126%
ERA 570 TPH Concentrations:	Soil Lot 1, D116-632	1,770 mg/Kg by Gravimetric 2,180 mg/Kg by IR			
	Soil Lot 2, D118-632	579 mg/Kg by Gravimetric 712 mg/Kg by IR			

This data is provided for guidance purposes only. UVF performed by Sitelab Corporation using three analyzers fitted with different ultraviolet light sources and optical filters. Crude oil calibrations performed using NIST SRM 2779 extracted in hexane with standards prepared in methanol. Factory calibrations performed using Sitelab calibration products listed for comparison.

Samples prepared using 10-g soil extracted in 20 mL methanol solvent for 24 hours. Spiked samples prepared using the oil. Percent recovery (%R) values account for concentrations in samples with no spike added.

Environmental Resource Associates (ERA) 570 TPH in Soil Certified Reference Material (CRM) analyzed using two lots with different composition. ERA uses vacuum pump oil in this product which dissolves poorly in methanol and is low in aromatic content, detected here with no spike added.

TABLE 5

**SPIKE RECOVERY ANALYSIS COMPARING THREE UVF ANALYZERS  
TESTING FRESH AND SALT WATER SPIKED WITH NIST SRM 2779 CRUDE OIL**

UVF Analyzers and Calibrations Performed		10 ppm Spiked Samples		20 ppm Spiked Samples	
		Fresh Water	Salt Water	Fresh Water	Salt Water
Samples Extracted Same Day and 10 Days After Preparation		Recovery %	Recovery %	Recovery %	Recovery %
<b>1. UVF-Trilogy, 255-nm UV with EDRO Optics:</b>					
Crude Oil Calibration, NIST SRM 2779	30 Minutes	101	95	88	89
	3 Hours	92	100	83	91
	10 Days	86	93	82	84
Factory Calibration, CAL-042H	30 Minutes	68	62	59	59
	3 Hours	60	67	54	61
	10 Days	57	62	55	56
<b>2. UVF-Trilogy, 365-nm UV with TPHOIL Optics:</b>					
Crude Oil Calibration, NIST SRM 2779	30 Minutes	100	94	92	95
	3 Hours	88	101	83	99
	10 Days	80	86	82	81
Factory Calibration, CAL-057H	30 Minutes	71	67	65	68
	3 Hours	63	72	59	70
	10 Days	57	61	58	58
<b>3. UVF-500D, 375-nm UV with Channel A Optics:</b>					
Crude Oil Calibration, NIST SRM 2779	30 Minutes	94	90	86	89
	3 Hours	81	96	76	97
	10 Days	78	81	80	77
Factory Calibration, CAL-056H-500D	30 Minutes	52	50	48	49
	3 Hours	45	53	42	54
	10 Days	43	45	44	43

This data is provided for guidance purposes only. UVF performed by Sitelab Corporation using three analyzers fitted with different ultraviolet light sources and optical filters. Crude oil calibrations performed using NIST SRM 2779 extracted in methanol with standards prepared in hexane. Factory calibrations performed using Sitelab calibration products listed for comparison.

TABLE 6

**AQUEOUS STABILITY ANALYSIS COMPARING THREE UVF ANALYZERS TESTING WATER SPIKED WITH NIST SRM 2779 CRUDE OIL WITHOUT SOLVENT EXTRACTION**

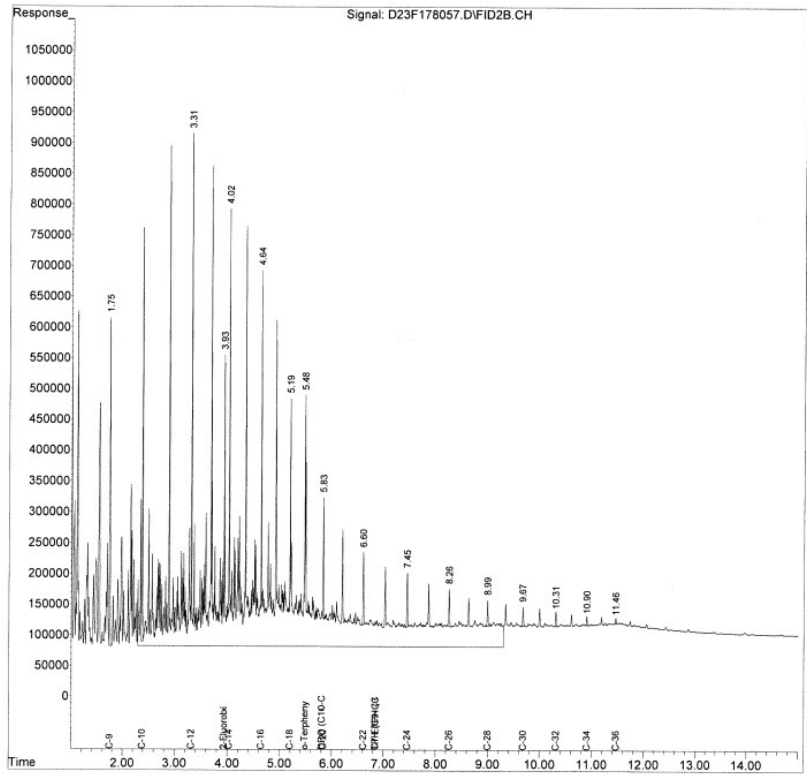
Analyzers Calibrated to NIST 2779 Crude Oil, Samples Tested Without Solvent Extraction Over Time	5 Min. mg/L	30 Min. mg/L	1 Hour mg/L	4 Hours mg/L	24 Hours mg/L	5 Days mg/L	10 Days mg/L	%Drop in Conc.
<b>1. UVF-Trilogy, 255-nm UV with EDRO Optics:</b>								
10 ppm Salt Water Spike	4.4	4.3	4.2	4.1	3.9	3.7	3.4	23%
20 ppm Salt Water Spike	7.2	7.0	6.8	6.6	5.9	5.6	5.2	28%
10 ppm Fresh Water Spike	5.9	5.8	5.8	5.6	4.4	3.6	3.4	42%
20 ppm Fresh Water Spike	9.5	9.3	9.3	8.8	6.2	5.1	5.0	47%
Salt Water, No Spike Added	0.0							
Fresh Water, No Spike Added	0.0							
<b>2. UVF-Trilogy, 365-nm UV with TPHOIL Optics:</b>								
10 ppm Salt Water Spike	17.5	17.1	16.6	16.7	15.0	14.0	12.4	29%
20 ppm Salt Water Spike	34.3	33.4	33.3	36.0	27.6	25.0	22.0	36%
10 ppm Fresh Water Spike	15.9	15.5	15.4	16.7	15.1	8.1	6.2	61%
20 ppm Fresh Water Spike	30.0	30.5	30.6	33.2	26.9	13.1	11.8	61%
Salt Water, No Spike Added	1.8							
Fresh Water, No Spike Added	0.7							
<b>2. UVF-500D, 375-nm UV with Channel A Optics:</b>								
10 ppm Salt Water Spike	16.8	16.1	15.9	16.4	14.1	13.5	12.4	26%
20 ppm Salt Water Spike	30.7	30.4	30.4	32.4	25.0	23.0	22.0	28%
10 ppm Fresh Water Spike	14.5	14.3	14.3	15.3	14.2	8.1	6.0	59%
20 ppm Fresh Water Spike	27.1	26.8	27.1	29.4	24.7	13.4	11.7	57%
Salt Water, No Spike Added	2.6							
Fresh Water, No Spike Added	1.6							

This data is provided for guidance purposes only. UVF performed by Sitelab Corporation using three analyzers fitted with different ultraviolet light sources and optical filters. Crude oil calibrations performed using NIST SRM 2779 oil extracted in methanol with standards prepared in hexane. %Drop in concentration calculated comparing sample results tested 5 minutes and 10 days after preparation.

In this study, samples were tested over time without solvent extraction to check sample degradation and to mimic fluorescence-based oil in water (OIW) monitors used to detect hydrocarbons in water continuously using flow cells, submersible probes or sensors. OIW monitors are calibrated to spiked water solutions using the source oil and the unspiked source water is used for the blank. As demonstrated here, spiked water samples used by OIW monitors to calibrate would perform best soon after preparation.

FIGURE 1

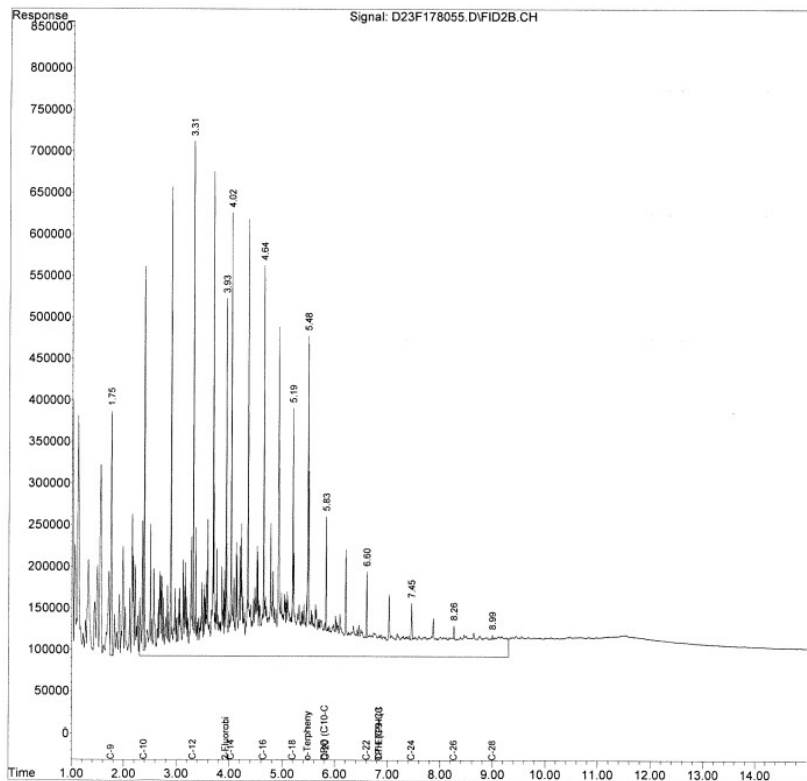
CHROMATOGRAM OF 10,000 PPM NIST SRM 2779 OIL EXTRACT IN HEXANE SOLVENT



Laboratory GC/FID 8015C  
TPH C9-C36 Concentration  
= 6,700 mg/Kg

FIGURE 2

CHROMATOGRAM OF 10,000 PPM NIST SRM 2779 OIL EXTRACT IN METHANOL SOLVENT



Laboratory GC/FID 8015C  
TPH C9-C36 Concentration  
= 4,600 mg/Kg