Improving NAPL Site Investigations using UVF and LIF Technologies Together

Image courtesy of Dakota Technologies, Inc.

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Technical Session: Life Cycle Risk Management in the Evaluation of NAPL Plumes

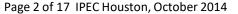
Tuesday, October 14th 1:15 PM – 1:40 PM



Environmental Issues and Solutions in Exploration, Production, Refining & Distribution of Petroleum

> October 14-16, 2014 Houston, Texas Marriott Westchase Hotel

What is Ultraviolet Fluorescence? How Does it Work?



What Fluoresces

Gasoline Jet Fuel Kerosene **Diesel Fuel** Home Heating Oil, No 2. Fuel Oil Heavy Fuel Oil, No. 6 Fuel Oil **Motor Oils** Waste Oils **Lubricating Oils** ✓ Cutting Oils **Transformer Oil Hydraulic Fluid Gas Condensates Drilling Muds & Drilling Fluids Crude Oils Bitumen, Tar Sands** Creosote, Coal Tars, Coal Ash

And What Doesn't

Fluorescence does not detect straight chain aliphatic hydrocarbons:

- PCE, TCE, dry cleaning solvents
 Other SVOC chlorinated solvents
- ✓ Methanol or Hexane used with test kits

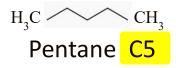


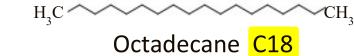
Popular UVF and LIF Applications

- Soil excavation and cleanup
- Site Assessments
- Remediation & Treatment
- UST Fuel Sites
- Oil Refineries, Pipeline Spills
- Power Plants, MGP Sites
- Military Sites, Airports
- Natural Disasters, Oil Spills
- Oil & Gas Production

Aliphatic Hydrocarbons

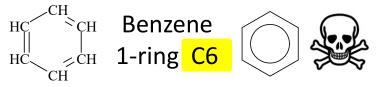
Saturated , Straight Chain Compounds (Alkenes)



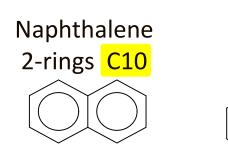


Aromatic Hydrocarbons

Unsaturated, Ring Shaped Compounds (Arenes)



BTEX: Benzene, Toluene, Ethylbenzene and Xylenes



Benzo [a] Pyrene 5 rings C20

PAHs: Polynuclear or Polycyclic Aromatic Hydrocarbons

TPH by GC-FID

Petroleum contaminants are split into different

Carbon Ranges or Fractions:

<u>Volatile Compounds</u> GRO, VPH, BTEX, VOCs: <u>C6-C10, C</u>5-C12 or C6-C12

Semi to Non-Volatile Compounds TPH, EPH, EDRO, ETPH, TRPH:

DRO:	ORO or RRO:	
C10-C28	C20-C35	
C12-C28	C25-C36	
	C28-C36	





UV Fluorescence detects <u>Aromatic</u> hydrocarbons over a wide range of petroleum contaminants

Fixed Wavelength Fluorometer (UVF) Photomultiplier Detector Samples are extracted **Converts Voltage to Concentration** in solvent using methanol or hexane. 0.25 ppm Soil, sediment, water, **NAPL or wipe samples** can be analyzed. **Emission Optical Filter Excitation UV Lamp energizes aromatic Optical Filter Glass cuvette contains** molecules at 254 nm sample extract or calibration standard

Portable Analyzers using Fluorescence



INSTRUMENT SPECIFICATIONS

Weight & Dimensions:	13 lbs (5.9 Kg); 11" x 9" x 8" (28 cm x 23 cm x 21 cm).		
Power Requirements:	External power supply, 100-120 VAC, Max. 30 watts.		
Operating Temperature:	45°F to 95°F; 7°C to 36°C.		
Principle of Operation:	Ultraviolet fluorescence spectrophotometer.		
Detector:	Factory-installed photomultiplier tube (PMT).		
Lamp:	Mercury vapor lamp included with analyzer (approx 10,000 Hr life expectancy). Replacement/spare lamps are available.		
Min. Detection Limits:	Varies depending on Sitelab Calibration Kit used; GRO 0.5 ppm, EDRO 0.1 ppm, PAHs 0.05 ppm and TPH-Oil 0.5 ppm.		
Display:	16 x 2 character LCD (3.9" x 0.9"; 9.8 cm x 2.2 cm).		
Data Output:	100% ASCII format through a 9-pin RS-232 serial cable at 9600 baud, USB adapter available, Part No. 3100-USB, sold separately		
Software:	Menu driven microprocessor-controlled. CD-ROM with software included for computer connection, Microsoft compatible.		
Filter Cylinder:	Accommodates up to eight, 25 mm (1-inch) round optical filters (up to 4 excitation and 4 emission filters).		
Cuvettes:	Includes cuvette adapter and two glass cuvettes. Replacement/ spare cuvettes are available.		
Readout:	Direct concentration (in ppm or ppb) or raw fluorescence.		
Calibration:	Multi-point calibration for direct concentration measurement.		
Blank:	Reads and subtracts blank using methanol or hexane solvents.		
Warranty:	One-year warranty, parts and labor.		
Approvals:	CE, UL and C-UL. ISO 9001 manufacturing. Made in USA.		



CONTAMINANTS

Ideal for gasoline, jet fuel, diesel fuel, heating oils, lubricating oils, crude oils, gas condensates, creosote, coal tars, coal ash and many other types of petroleum hydrocarbons.

QUICK RESULTS

Test soil, sediment or water samples in just 5 minutes using Sitelab test kits with solvent extraction.

ACCURACY

Correlates well to regulatory lab GC methods performed by certified laboratories. Ranked highest in U.S. EPA's "TPH in Soil" evaluation study. Publication No. EPA/600/R-01/080

FINGERPRINTING

Test BTEX and PAHs for forensic applications to determine the type or age of petroleum on your site.



Sitelab's UVF-3100A and UVF-3100D models include a field case with all the tools needed to perform tests.

The analyzer is fitted with optical filters sensitive to the gasoline range, diesel and oil range and Target PAH ranges. Sitelab's GRO, EDRO and PAH Calibration Kits provide fast, accurate measurement with quality control.

©2012 Sitelab Corporation All Rights Reserved UVF-3100 Analyzer Brochure Visit: site-lab.com Call Toll Free 877-SITELAB or Dial (USA) 978-363-2299 Sitelab Corporation • 86 Coffin Street • West Newbury • MA • 01985 • USA

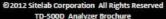


Petroleum Hydrocarbon Solutions



INSTRUMENT SPECIFICATIONS

Weight & Dimensions:	13.9 oz (0.4 Kg); 1.75" x 3.5" x 7.25" (4.5 cm x 8.9 cm x 18.4 cm).			
Power Requirements:				
a manufacture in the second second and protocols of sight	Four AAA batteries. Batteries good for approx. 1,000+ readings.			
Operating Temperature:	45°F to 95°F; 7°C to 36°C.			
Principle of Operation:	Hand-held ultraviolet fluorescence spectrophotometer.			
Detector:	Factory-installed photomultiplier sensor.			
Lamp:	Light Emitting Diode (LED).			
Min. Detection Limits:	Varies depending on Sitelab Calibration Kit used; TPH-Oil 5 ppm, Heavy PAHs 25 ppb.			
Display:	16 x 2 character LCD (2.5" x 0.6"; 6 cm x 1.5 cm); ppm or ppb units			
Data Output:	Not available. Record results manually.			
Automatic Power Down:	After 3 minutes of inactivity.			
Optical Filters:	Includes two sets of factory-installed excitation and emission			
	filters; use Channel A optics for Sitelab applications.			
Cuvettes:	Uses disposable 8 mm round glass cuvettes. Cuvettes are			
	included with Sitelab sample extraction kits and calibration kits.			
Calibration:	Single-point and blank.			
Blank:	Reads and subtracts blank using methanol or hexane solvents.			
Response Time:	5 Seconds.			
Diagnostics:	Displays percent fluorescence sensitivity of calibration and blank.			
Alarms:	Low battery, circuit failure, high blank.			
Warranty:	One-year warranty, parts and labor.			
Approvals:	CE, UL and C-UL. ISO 9001 manufacturing. Made in USA.			



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Manufactured for Sitelab Corporation by Turner Designs Hydrocarbon Instruments, Inc.

TD 500D

CONTAMINANTS Test samples for TPH with heavy fuel oils, waste oils or crude oils. Test for PAHs in old, weathered fuel oils, creosotes, coal tars and coal ash.

QUICK RESULTS

Test soil, sediment or water samples in just 5 minutes using Sitelab test kits with solvent extraction.



ACCURACY

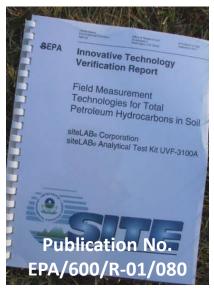
When used with Sitelab Calibration Kits, TPH-Oil results correlate well to EPA's 1644 gravimetric method. PAH results correlate well to EPA's 8270 method as sum of PAH compounds.



EASY TO USE The equipment is simple to operate. Sitelad's TD-5000 model includes a field case with all the tools needed to perform tests



Accuracy is Everything!



Evaluated by U.S. EPA in 2001

Ranked highest compared to other screening devices for TPH in soil.

Over 200 samples were tested. EPA spent \$800,000 on project.

Results were compared to split samples sent to certified lab for TPH analysis using 8015 by GC-FID.



GRO, EDRO & PAH Calibration Kits Certified calibration standards are specially formulated to correlate well to laboratory GC methods.



Sample Test Kits

Used to prepare and analyze soil, sediment or water using solvent extraction. Results take 5 minutes. Sitelab's popular UVF-3100D instrument is fitted with 3 sets of optical filters which are sensitive to different hydrocarbon ranges.







Laser Induced Fluorescence (LIF)



Laser-induced fluorescence (LIF) uses laser light to excite fluorescent molecules and is highly sensitive to non-aqueous phase liquids (NAPLs) in soil containing petroleum fuel oils, coal tars, creosotes, crude oils, etc.

A probe with sapphire window delivers short pulses of laser light by fiber optic cable into the soil below the ground. A detector simultaneously measures a time-resolved pulse of fluorescence at different wavelengths.



LIF probes are compatible with all direct push systems, like Geoprobe or CPT

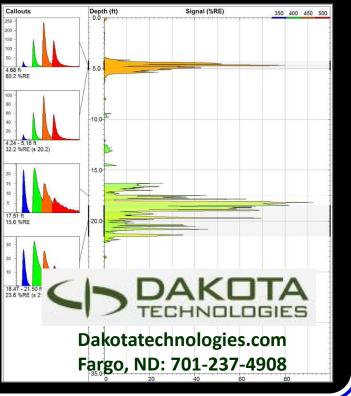
UVOST

For most petroleum applications.

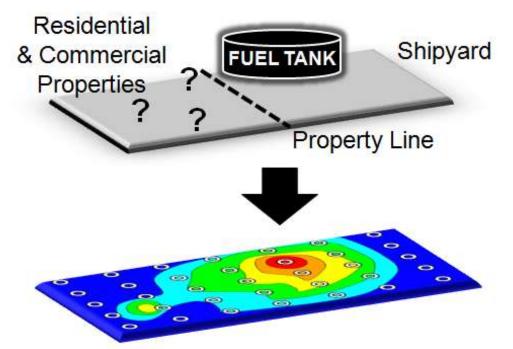
TARGOST For coal tars, creosote, heavy crude oil.

DyeLIF For DNAPL chlorinated solvent applications.





Example using UVF for Vertical Profiling



Site assessment is performed to investigate or remediate a property. Lab testing is required.

Field screening data is used to delineate the vertical and horizontal spread of contamination.

Off-site certified laboratories can be expensive with turnaround time taking 1 to 2 weeks.

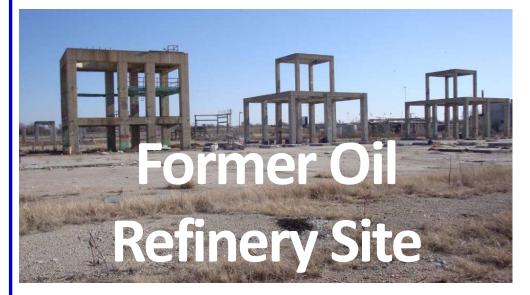
Soil Boring Depth (Ft) 6'-8' 100 8'-10' Δ 10'-12' 50 16,400 13'-14' 14'-16' 8,320 16'-17' 7,250 17'-18' 3,700 18'-19' 230 19'-20' 120 TPH (ppm)



Samples are collected from soil borings and tested on-site using UVF. Samples take 5 minutes to analyze.



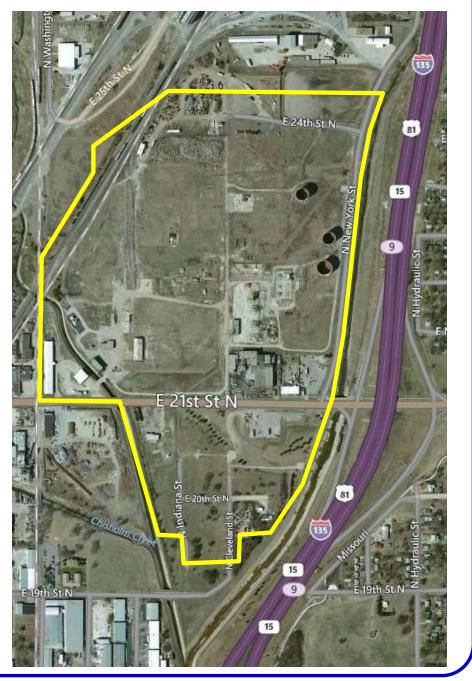
NAPL Investigation using UVF and LIF



Site has a huge 100-acre size plume of LNAPL commingled with gasoline, diesel, fuel oils, crude oil and other petroleum products.

Consultant uses Sitelab UVF to field screen 255 soils over 5 days testing for GRO, EPH, PAHs and TPH fingerprinting. A total of 1,020 results were reported on-site.

Samples were collected from 30 borings <u>next</u> to LIF locations performed 3 years prior.

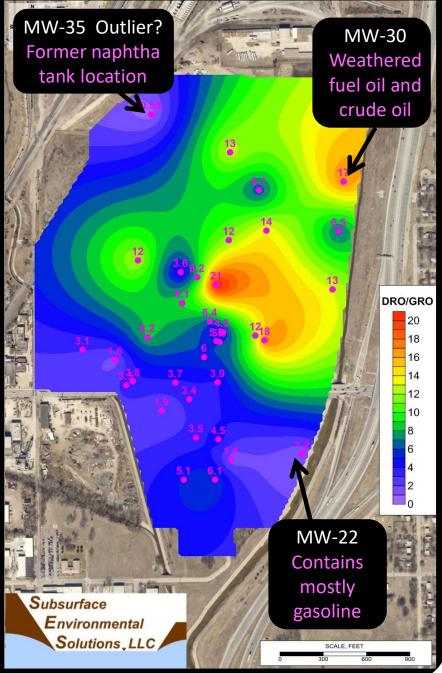


Fingerprinting NAPL Plume using UVF

UVF-3100 analyzer response testing oil samples collected from 35 monitoring wells. NAPLs diluted in solvent and measured at 10 ppm concentrations for both gasoline and diesel range hydrocarbons:



Examples at 10 ppm	GRO Response	DRO Response	DRO/GRO Ratios
MW-22	1.52 ppm	1.80 ppm	1.2
MW-30	0.73 ppm	12.5 ppm	17
MW-35	0.32 ppm	0.18 ppm	0.6



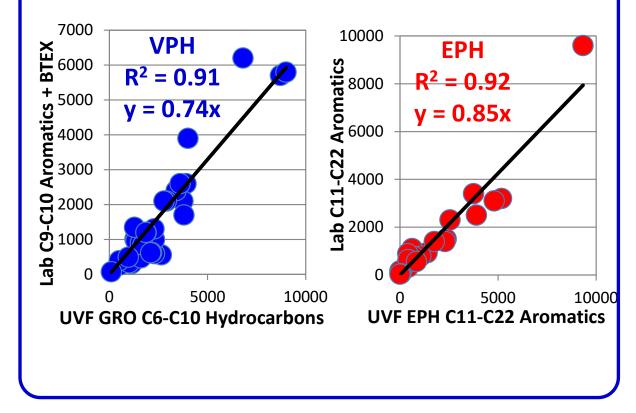
Page 11 of 17 IPEC Houston, October 2014

UVF Accuracy vs. Lab GC Results

A large number of soils collected from 30 borings were sent to a certified laboratory for confirmation analysis using the Mass DEP's VPH/EPH method. This method detects the aliphatic and aromatic hydrocarbon ranges separately.

Results correlated well, allowing the consultant to rely heavily on using the UVF results to convert LIF data to TPH concentration.

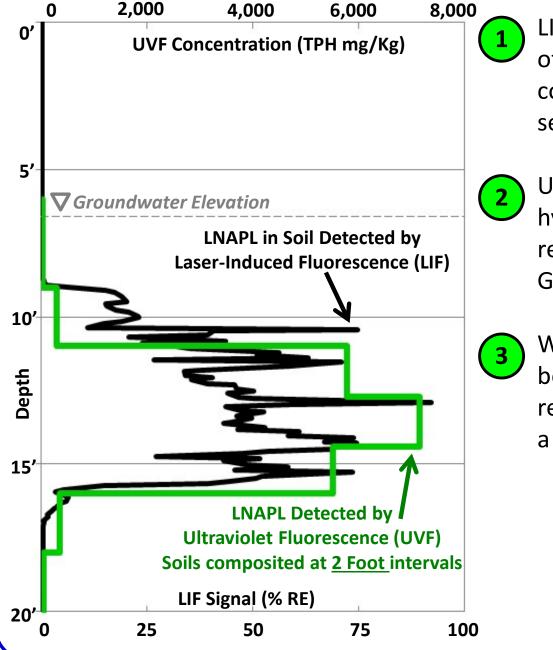
UVF-3100 vs. Laboratory GC-FID VPH/EPH Results Concentrations in ppm units (mg/Kg)





Calibration and sample test results can be recorded using UVF software Calibration standards are reusable and can be tested at any time to confirm calibration curve is linear

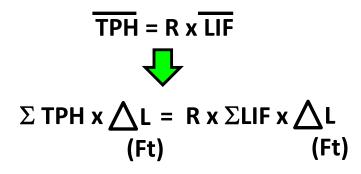
Calibrating LIF Response using UVF Data



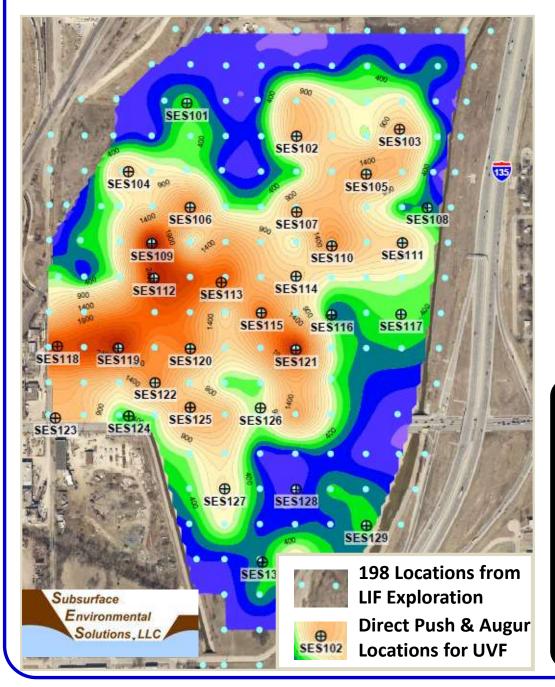
LIF provides real time, in-situ measurement of at 1-inch intervals without the need to collect samples. Results are <u>qualitative</u> or semi-quantitative in some cases.

UVF is a <u>quantitative</u> tool which measures hydrocarbons in a solvent extract. Test results correlate well to certified laboratory GC methods.

When used together, the LIF response can be converted to concentration using a response factor for a single-release site or a fancier formula for a commingled site:



Site Plan with UVF and LIF Locations

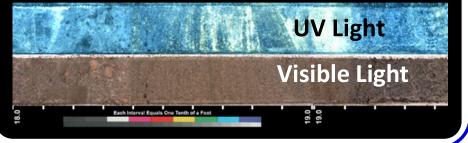


Consultant uses Surfer Software to create map showing extent of contamination.

Laboratory GC, UVF and LIF data is used to calculate the total mass of NAPL. This site has 6 million gallons of oil below the ground.

Previous estimates were 10 to 20 million gallons, based on invalid measurements such as product thickness.

Soil cores were also collected and frozen for physical testing: Centrifuge test measures residual oil saturation used to determine NAPL mobility and recovery.

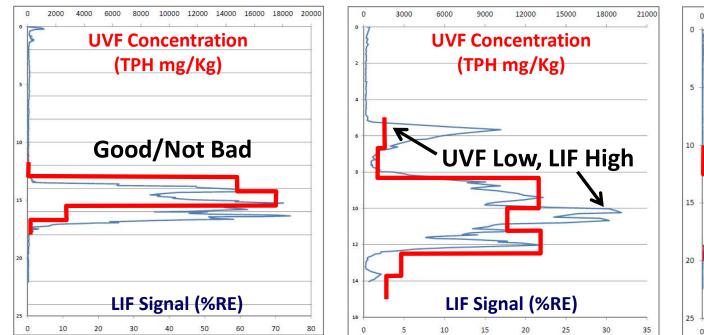


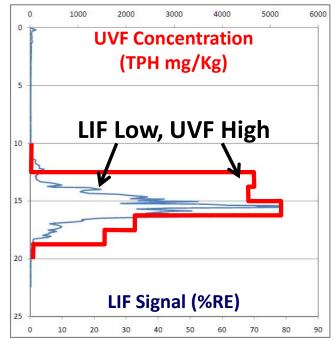
Page 14 of 17 IPEC Houston, October 2014

Challenges and Limitations using UVF and LIF Technologies



Jet Fuel Site Profiles Don't Match Up





Poor recovery in soil borings can sometimes occur skewing depth of TPH



NAPL may not be distributed evenly in intervals used to composite soils for UVF



End of Presentation Thank you





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