

# **Ultraviolet Induced Fluorescence Cone Penetration Testing for Characterization at Hydrocarbon Contaminated Sites for Natural Attenuation Studies**

**Kevin Biggar, Ph.D., P.Eng.**

Professor, University of Alberta, Department of Civil and Environmental Engineering, Edmonton, AB.

**David Woeller**

President, ConeTec, Vancouver, BC

**Sean Murphy, M.Sc.**

Environmental Soil Chemist, Komex International Ltd. Edmonton, AB.

**James Armstrong, M.Sc., P.Eng.**

Senior Hydrogeologist, Komex International, Calgary, AB.

**Abstract:** This paper describes a specially designed device for contaminated site investigations, the ultra violet induced fluorescence (UVIF) cone. The UVIF cone consists of a full piezo-cone penetrometer that can record tip resistance, sleeve friction, pore pressure and ultra violet induced fluorescence. Aromatic compounds in petroleum hydrocarbons (PHCs) will fluoresce in the presence of ultraviolet light. The UVIF module is located above the conventional piezo-cone and consists of a high intensity UVIF light projected through a sapphire window out into the surrounding soil and a photo multiplier tube sensor to record the fluorescence in the surrounding soil. The magnitude of the fluorescence relates to the relative concentration of the aromatic PHCs present in the soil. Data are presented to illustrate the potential of the UVIF-CPT for delineating PHC contaminant extent in the subsurface at upstream oil and gas facilities.

## **INTRODUCTION**

Delineating the lateral and vertical extent of hydrocarbon contamination in the subsurface at industrial sites is a routine component of environmental site characterization. One method of efficiently evaluating the extent of hydrocarbon contamination is through the use of ultra violet induced fluorescence (UVIF) cone penetration testing (CPT). The CPT provides a means of determining soil type, changes in soil stratigraphy, the location of the groundwater table along with various soil design parameters. A UVIF module can be coupled to the cone penetrometer, which enables the detection of aromatic hydrocarbons below the ground surface. The UVIF system operates on the principal that aromatic hydrocarbons (those containing one or more benzene rings) fluoresce when irradiated by ultra violet light. Therefore, by measuring the UVIF intensity in the subsurface one can determine both the lateral and vertical extent of PHC contamination.

## **Ultraviolet Induced Fluorescence**

Fluorescence spectrometry techniques have been used in the petroleum industry since the 1960's (Riecker, 1962). Some individual components of crude oil fluoresce within a

well-defined range of wavelengths (275-550 nm) when exposed to ultra violet light and this characteristic of crude oil was used to evaluate cores from early oil exploration wells.

Fluorescence spectrometry works on the principle that aromatic hydrocarbons fluoresce when illuminated by ultra violet light. The aromatic molecules absorb the UV light energy during radiation and immediately re-emit the light at a longer wavelength. This re-emission is termed fluorescence. On a molecular level, fluorescence involves atoms and molecules changing energy levels when excited with high-energy ultra violet light. Electrons in molecules exist at a set of specific energy levels. As a result of what is termed Coulombic interaction between protons and orbiting electrons, the electrons rest at their lowest energy orbital. When these electrons are excited with ultra violet light they are promoted to a higher, less stable energy level. Once the electron is promoted it tends to fall back to its original more stable energy level and in doing so, gives off energy by emitting a photon. This electronic transition and emission from high-energy state to low energy state is called fluorescence emission.

The difference between the excitation (250 nm) and emission (275-550 nm) wavelengths is called Stokes shift (refer to Figure 1). Specific hydrocarbon compounds can be identified by the magnitude of their Stokes shift. In general, as the number of aromatic rings increase the fluorescent response shifts toward longer wavelengths. Therefore, lighter compounds tend to fluoresce at shorter wavelengths and heavier compounds fluoresce at longer wavelengths.

## **UVIF-CPT**

The UVIF cone used for this study consists of a piezo cone with a UVIF module, as shown in Figure 2. The UVIF module contains a high intensity ultra violet light source as well as a fluorescence detection system. During penetration, measurements are made by illuminating the soil with an ultra violet light source through a clear sapphire window. The fluorescence emitted by the aromatics contained within the soil is detected in the probe by a small photo multiplier tube. The signal from the photo multiplier tube, measured in volts (V) is conducted through the electrical CPT cable to a data processing system in the CPT rig.

The UVIF system does not require any fiber-optic cables because the complete sensing system is located down-hole, in the probe. This feature is an advantage compared to the Laser Induced Fluorescence (LIF) system where a laser light source is transmitted via one fibre-optic cable from the surface to a sapphire window, and the fluorescence is transmitted via another fibre-optic cable back to the surface to a spectrometric analyzer.

A detection limit of approximately 15 mg/kg of dry weight for light nonaqueous phase liquids (LNAPL's) in soil is possible according to some researchers (Olie et.al. 1994). The intensity of the radiation emitted by the contaminant is an indication of the relative concentration of aromatics as well as the number or aromatic rings in the compounds. Figure 3 illustrates the variation in fluorescence intensity (Volts) with concentration of a diesel standard in ethanol. The detection system can be modified to optimize the

identification of specific contaminants by using filters to control the emission wavelength recorded (refer to Table 1).

**Table 1. Variation in Fluorescence Intensity for Different Polyaromatic Hydrocarbons and Emission Filters (Vertek, 1999)**

Sample	Fluorescence Intensity (V)	
	350 nm Filter	475+n m Filter
Clean Sand	0.01	0.01
Creosote (light extract)	<0.1	0.67
Creosote (heavy extract)	<0.1	1.00
Coal Tar (neat liquid)	<0.1	1.10
Crude Oil on Sand	3.1	1.0
Diesel on Sand	3.1	0.55
Unleaded Gasoline on Sand	6.3	0.83

Using current UVIF technology, contaminants can only be identified generically and only qualitative assessments are realistic. Elaborate analytical systems are being developed for LIF systems (Grundl *et.al*, 2002), but they are currently in the experimental stage, and significantly more expensive than the UVIF counterpart.

Control soundings are required at any site so that a background fluorescence intensity profile can be established, and if necessary, used to normalize the contaminant fluorescence profiles. Carbonates, humic materials and other organic matter are known to fluoresce, so their presence may possibly complicate analysis of response. Background fluorescence in soils is typically in the range of 0.6 to 0.9 V with the UVIF system used in this study. Changes in the fluorescence intensity profile caused by hydrocarbon contaminants can be successfully mapped both horizontally and vertically using the UVIF-CPT. Table 2 lists various contaminants that have been successfully mapped using the UVIF-CPT.

**Table 2. Hydrocarbons Detected Using Ultraviolet Induced Fluorescence**

Gasoline	Transformer Oil	Kerosene
Benzene	Diesel Fuel	Lubricating Oil
Hydraulic Fluid	Toluene	Aviation Fuel
Creosote	Turpentine	Ethyl benzene
Fuel Oil	Asphalt	Varsol
Naphthalene	Motor Oil	Tar

## UVIF-CPT AT UPSTREAM OIL AND GAS FACILITIES.

The UVIF-CPT has been used recently at a number of upstream oil and gas contaminated sites, in particular, flare pits and a gas condensate spill site. Flare pits are unlined earthen pits where waste fluids from facility operation are directed for burning. Typical fluids sent for flaring include crude oil and natural gas condensate, but may include other materials such as small volumes of produced water (brine), drain fluids, pigging waxes, and pop tank spillage. In areas where access was unrestricted these pits may also have been used as general waste repositories.

Natural gas condensate (condensate) refers to the hydrocarbon fraction separated from natural gas as a liquid at atmospheric levels of temperature and pressure. Condensate may contain a wide range of low molecular weight (C<sub>4</sub>-C<sub>12</sub>) hydrocarbons, including aliphatics (*i.e.*, butane, pentane, hexane, *etc.*), aromatics (benzene, toluene, ethylbenzene and xylenes), branched and cyclic compounds. These compounds are usually highly volatile, but may be found in liquid phase in the subsurface at some contaminated sites.

As previously described, it is hydrocarbons containing aromatic rings that fluoresce in the presence of ultraviolet light. Flare pit residues may contain significant aromatic constituents from crude oil, and as byproducts of incomplete combustion of PHCs sent to the flare pit.

A typical contaminated site investigation initially focuses analytical effort on target compounds that are regulated, usually because of their potential human health and environmental risk. Compounds of potential concern include the BTEX suite and selected aromatics. Some of these regulated compounds are shown in Figure 4.

Limiting analysis to typical target compounds can be misleading if it precludes other aromatic compounds that may contain substitutions of sulfur, oxygen, nitrogen, *etc.* for hydrogen atoms in the structure. Such substitutions can result from incomplete combustion of the parent aromatic compound found in the crude oil, or may be microbial metabolites of the parent compound resulting from in-situ biodegradation.

A previous study at the former flare pit discussed herein analyzed for the total fraction of aromatic compounds (including substituted compounds) in a contaminated soil sample adjacent to a flare pit. The analytical method is referred to as SARA analysis, (Saturates, Aromatics, Resins, and Asphaltenes). Table 3 shows the constituents of each component.

The high expense of SARA analysis means this approach is seldom used in routine contaminated site investigations. Of the above components, UV fluorescence may be attributable to the Aromatic and Polar 2 fraction. The SARA analysis of the soil adjacent to the former flare pit provided the following approximate fractions of the individual components: Saturates - 55%, Aromatics - 17%, Polar 1 - 9%, Polar 2 - 9%, Asphaltenes - <10%. The concentration of the total target, regulated aromatic compounds was much less than 1%. Given that the fluorescence using UVIF is attributable to the aromatic and polar 2 fraction, the UVIF approach may provide additional insight for hydrocarbon impact delineation.

**Table 3. SARA Analysis Elements**

Saturates	straight, branched and cyclic alkanes and alkenes
Aromatics	mono and polycyclic aromatic hydrocarbons lacking heteroatoms
Resins	
Polar 1	Low molecular weight amorphous polymers of various PHCs including alcohols, acids, and hydroxyacids, fatty acids
Polar 2	-N, and -S substituted heterocyclic aromatic compounds (pyrroles, quinolines, diazoles, carbazols, thiophenes, benzothiophenes, and thiozoles
Asphaltenes	Complex highly condensed, high molecular weight heterogeneous hydrocarbons including both aliphatic and aromatic structure. Very poorly characterized due to the lack of appropriate purification and separation technologies

**Case History #1: Flare pit in till**

UVIF-CPT was used to characterise petroleum hydrocarbon presence in the vicinity of a former flare pit. Numerous soil boreholes had been completed from 1996 – 2001, in addition to a number of groundwater monitoring wells to determine the extent of PHC presence at the site. The soil deposit in the area was predominantly silts and clays in a very heterogeneous deposit on Crown land. The soil in the immediate flare pit area was excavated to a maximum depth of 4 m bgs (approx. elev. 984 m) in 2001. Soil adjacent to the pit to a depth of 1.5 m was also excavated in 2001.

Despite the considerable amount of prior site characterisation, uncertainty remained as to the precise extent of free phase PHCs at the site. This information was necessary to plan and execute remedial activities relating to capture and removal of the free phase. UVIF-CPT technology was recommended to help better understand the free phase extent, and gain insight into the locally heterogeneous conditions that were affecting the product distribution.

Seventeen UVIF-CPT holes were advanced in the fall of 2002. These holes were carried out essentially in three concentric circles moving away from the source, with two test holes being located within the area of the former flare pit.

Figure 5 shows a cross-section based on 5 of the CPT holes, which progress downgradient from left to right. The figure illustrates the heterogeneity of the deposit along the transect. The deposit was also very heterogeneous perpendicular to the transect, so migration pathways could have been tortuous across the site. Superimposed on the interpreted soil stratigraphy are the UVIF profiles at the CPT locations. CPT2 shows very high UVIF response adjacent to the former flare pit, with readings going off scale (>10 V) from approximately 985 to 983m. These highest values appear to reside atop a stiff overconsolidated (OC) clay (till). The UVIF response of approximately 5 V

continues through this material, through a silty-clay and clay deposit, then ends abruptly atop a thin OC clay deposit at approximately 981 m.

Moving away from the former flare pit the UVIF response decreases dramatically in amplitude and vertical extent. At CPT9 maximum UVIF response is 2.5V, and resides primarily atop and within the upper region of the stiff OC clay approximately 3m below grade from 985 to 983m. The jagged nature of the UVIF implies that PHCs are likely resident in numerous discrete layers.

Approximately 40 to 50 m from the former flare pit the UVIF response shows PHCs in a relatively thin layer (20 - 50 cm thick) 2-3 m below grade atop a thin clay layer within a silty clay deposit. At CPT 13, the PHCs actually appear to have passed beneath a shallow monitoring well, and above the screen in a deep well, so went undetected. At CPT 15, free phase was observed nearby in the wall of an excavation for source removal of what was believed to have been a storage tank leak. The CPT-UVIF investigation suggests that the free phase at this location had actually emanated from the flare pit.

The CPT-UVIF investigation provided significant insight into the heterogeneity of the local deposit and its effect on the vertical and lateral distribution of free phase hydrocarbons that had emanated from a former flare pit.

### **Case History #2: Natural gas condensates in a silty sand**

The UVIF-CPT system was also used at a natural gas processing facility where a layer of free phase gas condensate was known to exist over a portion of the site. The soil profile had previously been classified as a silty sand grading to a sandy silt to greater than 8 m below ground surface. The purpose of the UVIF-CPT survey was to improve lateral and vertical delineation of the free phase condensate to assist in the design of a hydrocarbon recovery system. A secondary goal was to gain insight into the geologic variability from the CPT data.

A typical UVIF-CPT plot is shown in Figure 6. This hole was installed adjacent to a monitoring well where free phase had been measured from a depth of approximately 4.6 to 6.0 m below ground surface (mbgs). In contrast, the UVIF signal shows a slight increase from a background value of approximately 0.8V to maximum of approximately 1.0 V over the depth interval from 4.1 mbgs to approximately 5.7 mbgs. This muted response may be contrasted to the values of 2.5V to >10V recorded at the flare pit discussed above. It is speculated that the low aromatic and aromatic compound content of the gas condensate rendered the UVIF system unreliable for delineating the extent of the free phase gas condensate at the site.

### **CLOSURE**

The UVIF-CPT provides another powerful tool in the suite of systems that can be used by the professional to cost-effectively characterize contaminated sites. It was found to provide excellent results in the delineation of PHC contamination emanating from a flare pit associated with oil and gas production. It did not, however, provide the desired

resolution when used to track the extent of a natural gas condensate plume. This experience underscores the importance of working with the providers of the UVIF equipment early on during the proposed use of the technology. It is beneficial to have soil samples contaminated with compounds of concern sent to the UVIF providers for preliminary assessment of the response to evaluate if the UVIF system will provide the desired results.

## **REFERENCES**

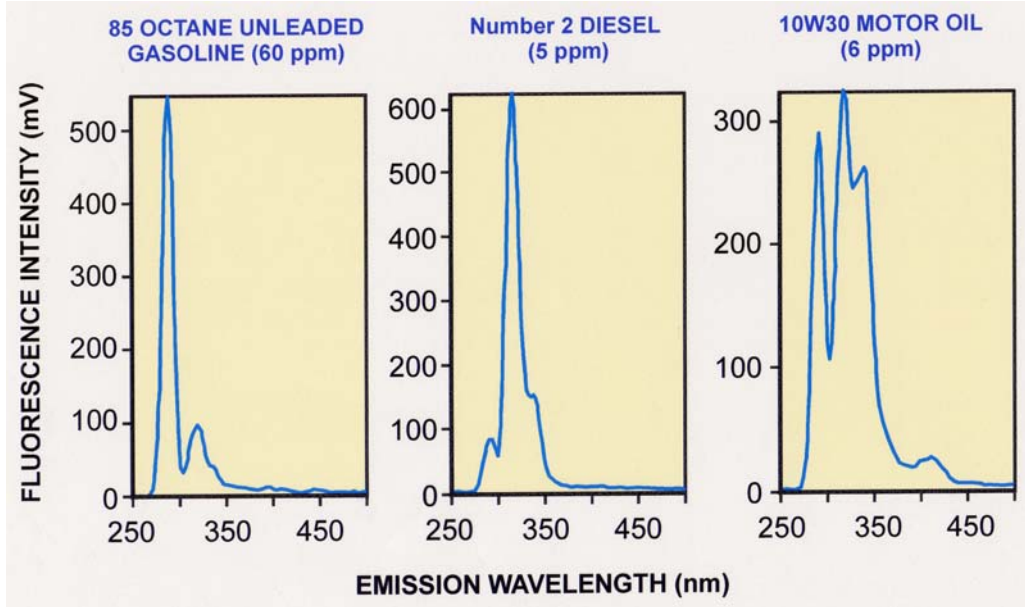
Grundl, T.J., Aldstadt, J.H., Harb, J.C., St. Germain, R.W., and Schweitzer, R.C., Demonstration of a method for the direct determination of polycyclic aromatic hydrocarbons in submerged sediments. Environmental Science and Technology. (Pending printing)

Olie, J.J., Meijer, J.C. and Visser, 1994. Status report on in situ detection of NAPL-layers of petroleum products with Oil Prospecting Probe Mark 1.

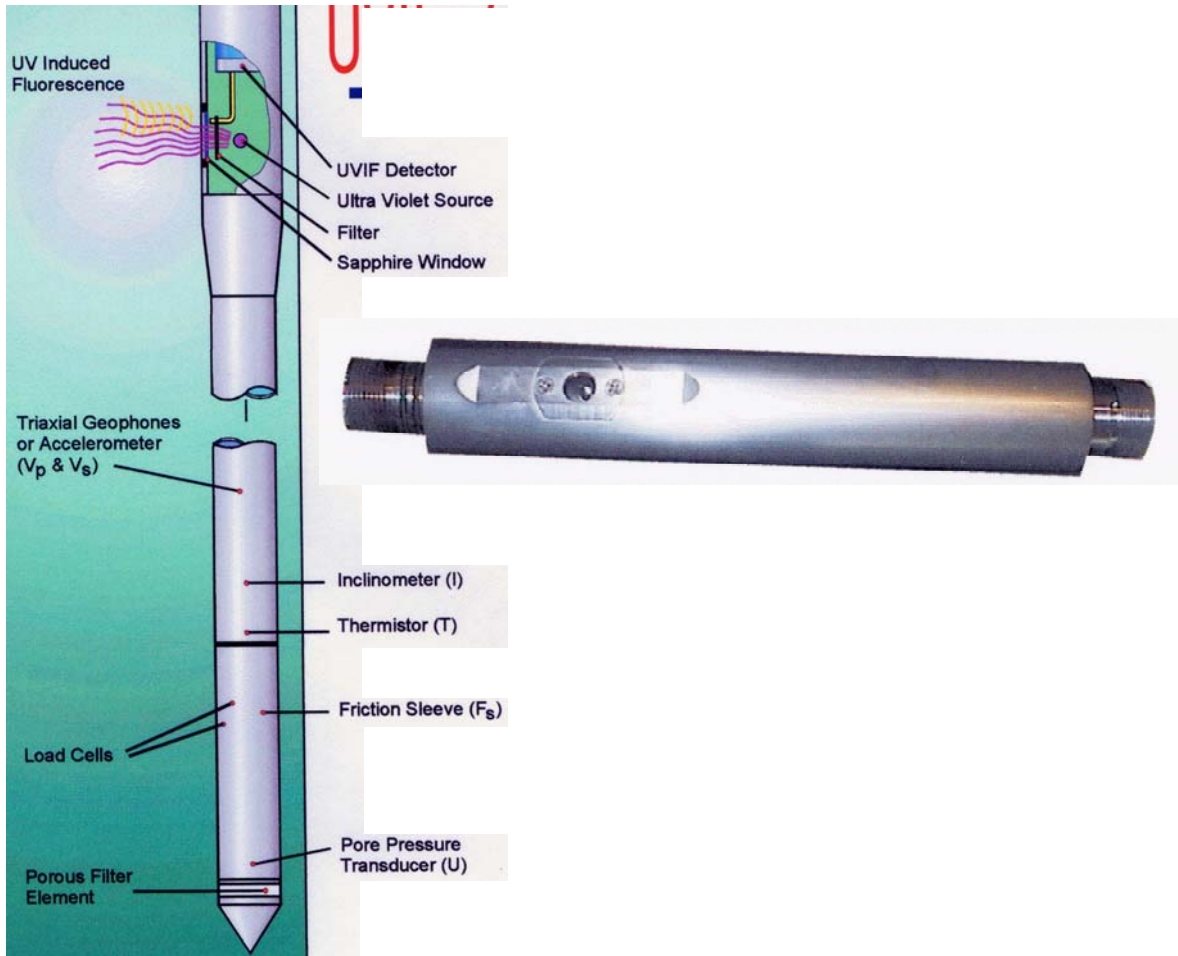
Riecker, R.E. 1962. Hydrocarbon fluorescence and migration of petroleum. Bulletin of the American Association of Petroleum Geologists. V. 46:60-75.

Vertek, 1999 Product Literature.

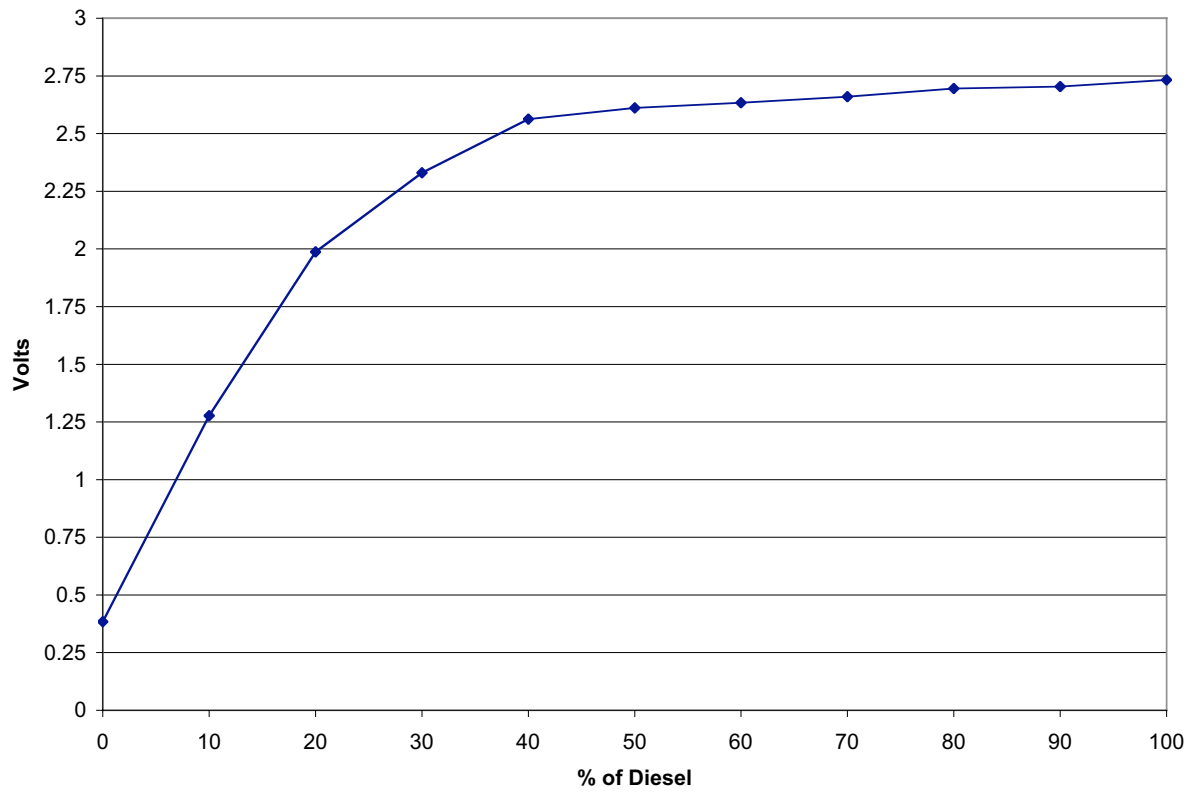
**Figure 1: Ultraviolet induced fluorescence emission wavelengths**



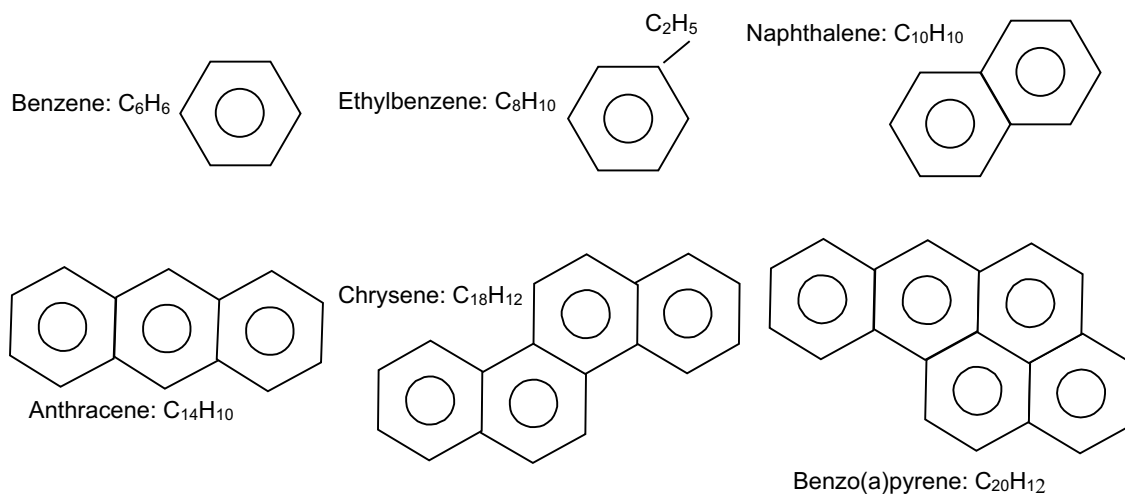
**Fig 2. UVIF CPT schematic and UVIF module photo**



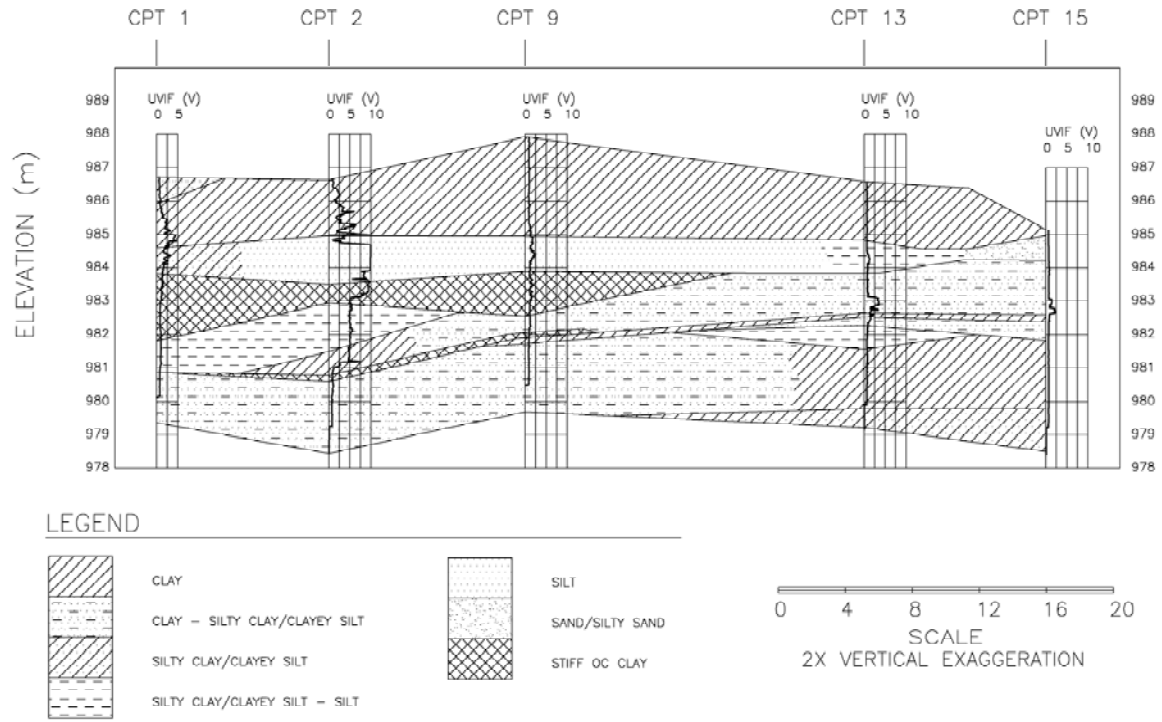
**Figure 3. Variation in fluorescence intensity (Volts) with concentration of a diesel standard in ethanol**



**Figure 4. Some typical regulated aromatic hydrocarbon compounds**



**Figure 5. Cross section showing stratigraphy and UVIF profiles at former flare pit site.**



**Figure 6. UVIF-CPT output for natural gas condensate contaminated site.**

