

## What is crude oil?

Crude Oil or Petroleum, is simply unprocessed oil found deep beneath the earth's surface. It can range in color from clear to black and can be found as a liquid or solid. Overall properties of crude oils are dependent upon their chemical composition and structure. Crude oil is pumped and stored in barrels for future refinement. The refinement process may involve filtering, addition of additives, and specialized separation techniques to create specific crude oils and crude oil products. Generally all crude oils are made up of hydrocarbon compounds. The main hydrocarbons found in crude oil are Aliphatics, Alicyclics, and Polycyclic Aromatic Hydrocarbons (PAH)

### Aliphatics and Alicyclics Properties

- Quickly broken down by natural processes
- Residence time in environment is less than a day
- Straight chain or ring carbon structures with weak bonds
- Low fluorescence characteristic

### Polycyclic Aromatic Hydrocarbons (PAH) Properties

- Most abundant of the main hydrocarbons found in crude oils
- Many are toxic
- Can be carcinogenic to plants and animals
- Difficult to separate from water using regular filtering techniques making them a potential human health hazard
- 6-sided carbon rings which contain strong bonds
- Prolonged breakdown by natural processes
- Highly fluorescent aromatic characteristics allow researchers to easily detect PAH's using fluorescence techniques

The aromatic carbon compounds (**PAH's**) found in crude oils can range from simple structures like Naphthalene to very complex ones like Asphaltene (Figures 1A and 1B). The **Aromaticity** of the compound plays a key role in determining its fluorescence intensity. There are other factors that also affect the fluorescence properties of crude oils.

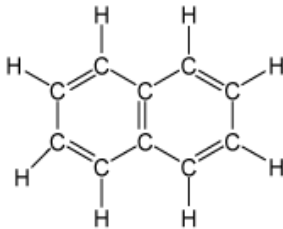


Figure 1A: Naphthalene

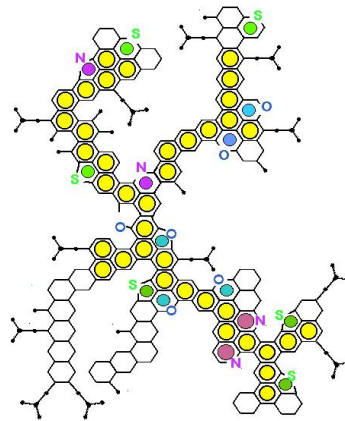
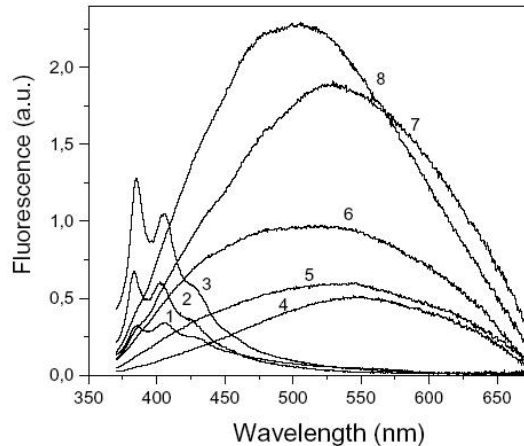


Figure 1B: Asphaltene

## Fluorescence of oil

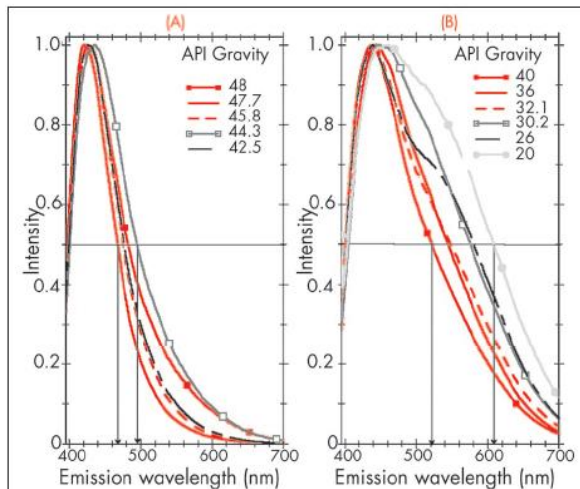
Oils are typically excited using ultraviolet wavelengths (300-400 nm) and fluoresce in the visible wavelength range from 400-600 nm. The compound's **Carbon Structure** will determine its fluorescent properties. The addition of **Additives** will also affect the fluorescence properties of oils. Figure 2 is a graph taken from Karpicz et. al. showing different types of refined crude oils and crude oil products, each with its corresponding emission wavelength. The difference in crude oil fluorescence is primarily due to the refinement process.



**Figure 2 Legend:**

- 1 – Motor oil
- 2 – Shell Diala oil
- 3 – Oil SAE 30
- 4 – Bunker Fuel oil
- 5 – Arabian Medium crude oil
- 6 – Basra crude oil
- 7 – German crude oil
- 8 – Nihian crude oil

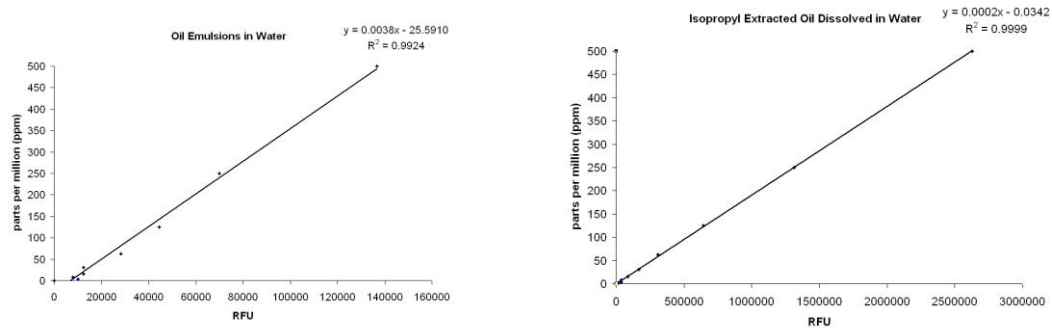
Physical properties such as **Weight** of oil or **API gravity**, a term used to express the density of petroleum liquids, may also affect the fluorescence of crude oils. Figure 3 from Ryder, Iwanski & Montanari (2004) compares the emission wavelength of two weight classes of crude oils. Type A oil is light oil and type B is medium heavy oil. Heavier oils with lower API gravity tend to shift towards the red end of the light spectrum and have broader peaks.



**Figure 3:** (A) is light oil, (B) is medium heavy oil. Excitation light being used is 380nm. Both oils are obtained from the North Sea.

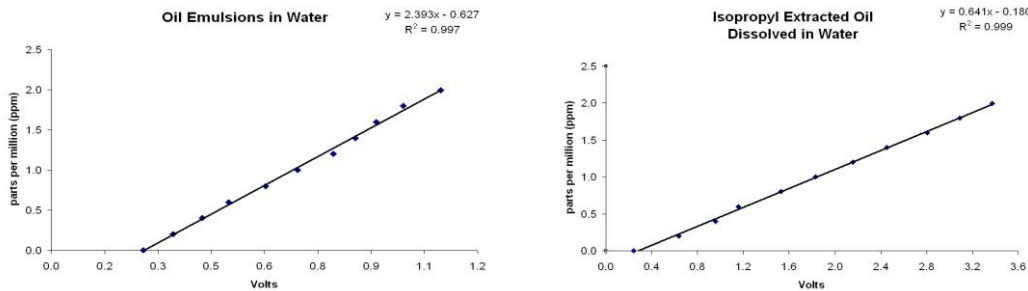
Turner Designs **10-AU**, **Trilogy**, and **Cyclops-7 fluorometers** are able to detect the fluorescence of crude oils or crude oil products. Natural water samples are excited at a specific ultraviolet wavelength of light. Specialized band pass emission filters allow the instruments to read a broad range of dissolved oil compounds or emulsions in water.

Figure 4 shows preliminary data gathered from the Trilogy fluorometer. Crude Oil dilutions were used to check if linearity was comparable for dissolved oil and oil emulsions in water to 500ppm.



**Figure 4:** Comparing linearity of oil in water and dissolved oil in water using Trilogy fluorometer. Crude oil dilutions of concentrations from 0-500ppm were used. Good linearity was achieved for both data sets ( $r^2=0.99$ ).

Resolution of the lower end can sometimes be difficult because of the inherent noise level of some systems. Figure 5 looks at how the Cyclops-7 resolves lower end concentrations of dissolved oil in water and oil emulsions in water. As a result of the low signal variation our detection limit is <0.1ppm. Crude oil concentrations reported in environmental systems are rarely found at the 0.1ppm level (Wilhelm & Spitz 2003).



**Figure 5:** Lower end resolution comparing oil in water and dissolved oil in water. Crude oil dilutions were used to establish linear responses for low concentrations ( $r^2 = 0.99$ ).

**Reference:**

A.G. Ryder, P. Iwanski, and L. Montanari "Fluorescence emission from petroleum; a valuable information source for petroleum analysis" Tpoint (in-house journal for EniTecnologie), 2-June, 9-14, (2004)

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