Water Fearing
Reliable Monitoring of Oil in Water

Numerous industries are regulated by authorities for monitoring oil in water. Any contamination of e.g. surface water with oil can massively harm flora and fauna. Due to the diverse characteristics of oil, fat and grease it is one of the toughest applications on the market. Hence, versatile and reliable online measurements are required to protect the environment.

> "Hundreds of LAR's analysers are successfully in operation to monitor water streams polluted by various oils to protect the environment, detect product spills and save costs."

Generally, oil is a collective term for viscous liquids with a high hydrogen and carbon content. It is a chemical substance that is hydrophobic and hence, immiscible with water (literally "water fearing"). On the other site, it is lipophilic and tend to dissolve in other liophilic substances as fats, oils, and lipids (literally "fat-loving"). Oil is of animal, petrochemical, or vegetable origin and is used in a wide area of applications. Typically, oil-in-water (OIW) applications are storm water runoff, hydrocarbon storage facilities, ground water reclamation sites, power plants and boiler condensate and cooling water reclaiming systems, water discharge into municipal water treatment systems, effluent monitoring and oil reclamation systems. At industrial sites that use oil for the production and processing of e.g. biofuels, lubricants and edible oils there is always the possibility of a leakage resulting in pollution of the plant, water systems, or other places. Hence, the need for OIW monitoring of storm and rain water runoffs is of great importance to prevent any pollution of the environment. A great deal of the expenses that are entailed by an oil spill and the attempt to treat the polluted water can be saved with help of an online oil-in-water analyser. A variety of these online analysers are available on the market. The selection of an oil-in-water process analyser can, however, be very problematic. Most of the available OIW methods measure oil indirectly resulting in the limited measurement of only specific oil characteristics. The oil consistency, composition and its origin all affect the analytical outcome. For every oil-in-water type the results need to be correlated to the applicable oil-in-water laboratory method. It gets really challenging when the OIW composition varies over time and contains a mix of different unknown types of oils.

Indirect OIW analysis methods: Fluorescence method

The oil-in-water fluorescent analyser measures the emitted light of Polycyclic Aromatic Hydrocarbons (PAH) that are commonly present in mineral oil. Examples of PAH are: benzene, toluene, ethyl benzene, xylenes and phenol. The method uses a light source such as a laser and the PAH's fluoresce in the presence of short-wave light. A mineral oil is a natural product with a unique composition. A specific oil type can consist of over a 100 different single components. Therefore, each oil type has a unique fluorescent fingerprint meaning it emits a certain amount of light at different wavelengths. The emitted fluorescence intensity is measured by a photo multiplier tube. The oil fingerprint is measured via a spectrophotometer. It is possible to determine the correlation of single oil type measurements against the applicable OIW laboratory analysis. Fingerprints of specific oil types, including their belonging calibration curves, are stored in a databank. A specific oil type is recognised when the fingerprint of the online analysis is identical to the stored oil spectra. However, this sophisticated optical computer technique will be of no help when the water contains a mixture of different oil types. Moreover, the fluorescence method is an indirect measurement. It can only be used for oils that contain PAH's. The size distribution of oil droplets will affect the OIW-measuring results. Often, a time consuming correlation study needs to be done. As oils wear-out over time, their fluorescence spectrum changes significantly. Therefore, the fluorescence method is not necessarily suitable for applications with waste water containing a variety of oil types, such as at refinery or oil terminal. None of the petroleum oil types are fluoresce at all and cannot be measured with the UV-fluorescence method.

A typical application is: Monitoring of the oil contamination level of overboard water at offshore oil winning platforms and Floating Production, Storage and Offloading (FPSO's) units.

	Oil and other hydrocarbons in water					
On-line analytical method	Mineral Oil Petroleum Oils			non-oil organic hydro carbons	Interference by	
	Dissolved Mainly aromatics	Dispersed; small oil droplets	Droplets Large oil droplets	Any physical phase	Small particles	Small gas bubbles
Fluorescence	Only if PAH's are present	Only if PAH's are present	Only if PAH's are present		OIW-signal interference by secondary fluorescence	OIW-signal interference by secondary fluorescence
Light scattering		OIW-signal depends on droplet size			Signal responds like being oil	Signal responds like being oil
UV-VIS / NIR / IR absorption	Signal span depends on absorption coefficient					
Total Organic Carbon						

	Results need to be correlated via laboratory analysis
	Results are absolute, no correlation required. Calibration is easy and fast
	Unwanted results and interference of OIW measurements

Figure 1: Oil-in-Water Methods and Selectivity, Copyright: Piet Broertjes

Author/Contact Details:
Dr. Werner Arts, President
LAR Process Analysers AG
Neukoellnische Alle 134
12057 Berlin
Tel: +49 30 278958-59
Email: sales@lar.com

Scattered Light Principle

The scattered light principle is capable of measuring oil as long as it is present as small dispersed oil droplets. A light beam propagates into a measuring cell and hits the dispersed tiny oil droplets. Some of this light will scatter. The intensity of the scattered light is measured by an optical receiver and the outcome is correlated to an oil standard. The optical bench is not that complicated. It consists of up to three light sources, each emitting a specific wavelength into a measuring cell. Furthermore, there are up to 5 light receivers (optical sensors) that measure the intensity of the scattered light. Light sources and light receivers are orientated in a specific angular configuration surrounding the measuring cell. It is a known fact that also small particles and gas bubbles will cause light to scatter. This same scattering method is used to measure turbidity and solids in water. Some manufacturers claim that their sophisticated optics and smart processors are able to distinguish between oil droplets and particles making their OIW-analysers ideal for selecting oil. An optimum scattering can be achieved at a droplet size of 1 to 10 micrometer. Ten big droplets of oil give a totally different measuring result than the same amount of oil dispersed into 10,000 tiny droplets. Scattered light OIW-analysers need quite a lot of mechanical pretreatment when attempting to condition the oil droplet size. Furthermore, these systems need a mechanism like a wiper or ultrasonic transducer to remove sticky oil fouling the optical windows of the measuring cell. If the oil is totally dissolved, and no oil droplets are present, then there is no oil reading at all. As it is an indirect method, the analyser results must be correlated to a laboratory-OIW method.

A typical application is: Monitoring oil in bilge water at marine applications.

Spectroscopy / Light Absorption Method

Many dissolved organics absorb light, e.g in the near infrared (NIR), infrared (IR), visible (VIS) or ultra violet (UV) spectra. Oil droplets cannot be measured via a light absorption method. Basically, the OIW-analyser or OIW-probe consist of a light source, an optical cell or an optical path and an optical receiver like a photo diode. Beer-Lamberts Law described the mathematical relation of the dissolved oil concentration in respect of the specific absorption coefficient, the emitted light intensity, the measured light intensity and the optical path length. Normally, oils have a high absorption coefficient meaning that the optical path length needs to be within the range of a few millimetres. Absorption spectra are measured by use of a spectrophotometer. A correlation of the measuring results against normalized laboratory measurements is needed. Many dissolved organic carbon species will interfere with the measurement. It is far from selective and the fouling of the optics by sticky oil causes intensive maintenance. The light absorption method is hardly applicable for online usage.

A typical application is: Monitoring of clean water with dissolved oils in a relatively low range.

Direct OIW-Analysis Method - Total Organic Carbon Analysis (TOC)

A TOC-analyser measures all types of oil, fat and grease regardless whether it is of mineral, petroleum, vegetable, animal or synthetic origin. Actually, the TOC-method is a carbon counting method. It is a so-called sum parameter analysis and responds to all organic hydrocarbon species. As it is a direct measuring method, based on the oxidation of organic hydrocarbons in an oxidising atmosphere, its outcome is defined by a chemical oxidation equation. On the other hand, the TOC-method is not, and cannot be made, selective to exclusively oily and fatty hydrocarbons. For many applications the OIW-analyser does not have to be "oil selective" simply because no other organic components than oil are present in that type of water. In general, the TOC-method is particularly suitable to monitor storm water and rainwater runoff, spill detection, shock loading, boiler feed water, return condensate and influent analysis of refineries, oil terminals, oil blending facilities and more. Some understanding of the types of processes and the types of components in that specific water stream is needed. Presuming that the oil-in-water alarm level is significantly high compared to the background level of non-oily hydrocarbons, the TOC-method should be considered as the preferable method. It offers many great features and advantages.

For an accurate TOC measurement, however, the sample take-off is of great importance. Oil and fats can be present as an oil slick or sheen, as dispersed oil, emulsified, in a dissolved state and as particles as big as lumps. Oils and fats are normally lighter than water and tend to float on the surface, oils with a higher density sink. The key to obtain a representative sample is to collect the sample from an area where it is vigorously mixed. In an ideal situation the water flows rapidly and is completely turbulent, consequently oil and water are mixed thoroughly. If such a location is not available, then we advise to create a turbulent mixed mass of water by use of a big industrial submersible impeller pump. This industrial pump will grind, mix and homogenise the water.

Most TOC analysers have a limit of detection of 2,000 mg/l. For the determination of higher ranges the sample must be diluted with demineralised water. Due to the hydrophobic characteristics of oil, they are not applicable. Furthermore, oils and fats cause absorption and adsoprtion on wetted parts leading to carry-over and memory effects. They then decrease the response time resulting in a slower recovery after a peak contamination. Therefore, only systems that have little wetted surfaces and work without dilution can be used. LAR's analysers do not need any dilution of the sample. There are only three wetted parts in the anaylser that are in contact with the sample: The sample tube, a quartz vessel and the injection needle. After every measurement cycle these parts are being flushed with clean water. The entire oxidation power of the QuickTOCultra ranges up to 50,000 mg/l TOC. Thus, LAR's ultra high temperature combustion at 1,200°C is way ahead of common thermal oxidation methods. The continuous online analysis of oils and fats in waste water is known to be one of the toughest applications. Most oil-in-water analysers have trouble handling this highly contaminated oily and fatty waste water. They use numerous wetted components that are rapidly fouled and contaminated causing analytical memory problems, as well as requiring unacceptable maintenance due to clogging issues.

LAR's QuickTOCultra-analyser is an exception. It has proved to be very accurate and reliable. LAR offers well conceptualised oil-in-water analyser installations consisting of an innovative sample take-off technique, sample transfer, anti-isokenetic sampler and TC/TOC/TOD-analyser. Additionally, a two stream application offers the great feature of monitoring the influent and effluent waste water loads simultaneously and thus determining the efficiency of the WWTPs operation. In particular, the analyser is able to measure up to six stream in one unit. In essence, the technique used is based on four simple rules: Keep it hot, keep it unblocked, keep it simple and keep it clean.

Figure 3: QuickTOCultra analyser provides reliable and fast OIW measurements, Copyright: LAR AG

Summary

Common OIW-analysers measure indirectly, basing results on secondary oil characteristics. In contrast, a TOC analyser measures directly. It is a carbon counter and is not influenced by oil type or consistency. LAR's QuickTOCultra proves to be very suitable for OIW applications, offering a dynamic measurement range from 10 up to 50,000 mg C/l and a complete well-designed sample take-off and sample transfer system, as an essential and integral part of its complete package. Hundreds of LAR's analysers are successfully in operation to monitor water streams polluted by various oils to protect the environment, detect product spills and save costs.

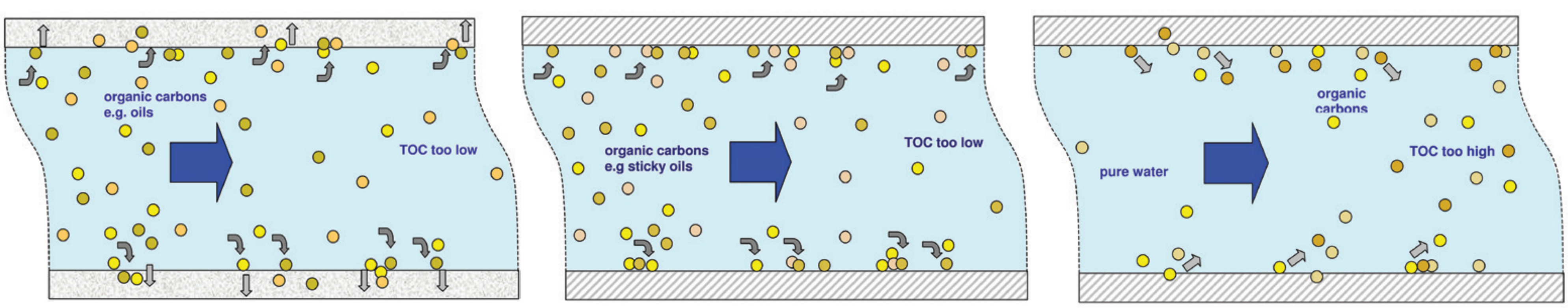

Figure 2: Absorption, adsorption, desorption lead to memory and carry-over effects