Hydrocarbon in Water Monitors Using Fluorescence

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ABSTRACT

Quick and reliable monitoring for hydrocarbons in wastewater, cooling and heating water is valuable to industrial facilities. Water monitors using fluorescence are capable of detecting hydrocarbon concentrations in water as low as 5 µg · L^{-1}, and can thus give operators an early warning of oil leaks and spills, allowing costly repairs, cleanup and fines to be avoided. This paper introduces the fluorescence monitors and presents data from recent studies to illustrate the detection levels of the technology.

INTRODUCTION

Water monitors using fluorescence are capable of detecting hydrocarbon concentrations in water as low as 5 µg · L^{-1} and as high as 10 000 mg · L^{-1} depending on the application. Because only the target hydrocarbons fluoresce, these monitors have no significant measurement effect from turbidity or suspended solids (rust, dirt, gas bubbles, soot, etc.). Fluorescence monitors provide a measurement that is linear with hydrocarbon concentration and are more accurate than the typical laboratory methods used to measure hydrocarbon concentration in plant discharge water.

This technology is ideal for monitoring leaking lube oil, fuel oil, hydraulic oil and electro-hydraulic control fluid in storm water, cooling water, steam condensate loops and boiler feedwater. It gives the earliest warning of leaking heat exchangers of any technology available on the market. This early warning has allowed plants to prevent excess hydrocarbons from entering boilers, being exposed to the atmosphere in cooling towers, and being discharged to the sewer or environment in wastewater or open-loop cooling systems. Data from recent studies will be presented to illustrate the detection levels of the technology.

HYDROCARBON FLUORESCENCE

Aromatic fractions of oil found in industrial water can be stimulated, or excited, with ultraviolet or near-ultraviolet light to emit fluorescent light. The process is illustrated in Figure 1. Excitation light is directed to a sample at a wavelength, λ_{EX}. The aromatic molecules in the sample absorb the excitation light and rise from their normal energy level (E_0, ground state) to an excited energy state, E_2. The excited molecules then lose their absorbed energy (relaxation) by a variety of mechanisms and reduce to a lower energy state, E_1. The molecules then return to E_0 by emitting a photon of fluorescent light at a wavelength λ_{EM}. The energy emitted by fluorescence ($E_1 - E_0$) is lower than the energy absorbed ($E_2 - E_0$). Since light energy is inversely proportional to wavelength, the wavelength of the emitted fluorescent light, λ_{EM}, is always longer than the wavelength of the excitation light, λ_{EX}. The intensity of the fluorescence emission, I_F, is proportional to the concentration of the fluorescent molecules in the sample.

Fluorescence is extremely sensitive to hydrocarbons in water, capable of monitoring most oils in industrial water at concentrations less than 1 mg · L^{-1} and providing a linear response over the desired concentration range. Turner Designs Hydrocarbon Instruments, Inc. manufactures several types of process fluorometers, and markets the Jorin online particle analyzers. Some oil-in-water monitors are hand held grab sample analyzers and others are low maintenance continuous online monitors.

As examples of fluorescence sensitivity, heavy fuel oil #6 can be detected at as low as 5 mg · L^{-1} in steam condensate and most turbine lube oils and electro-hydraulic control fluids have a detection limit that ranges from below 0.1 mg · L^{-1} to 2 mg · L^{-1}.

WATER ISSUES

Industrial Wastewater

Industrial facilities, like power plants, using petroleum products for fuel, lubrication or other purposes have the potential to pollute if oil spills or leaks get into the rain-

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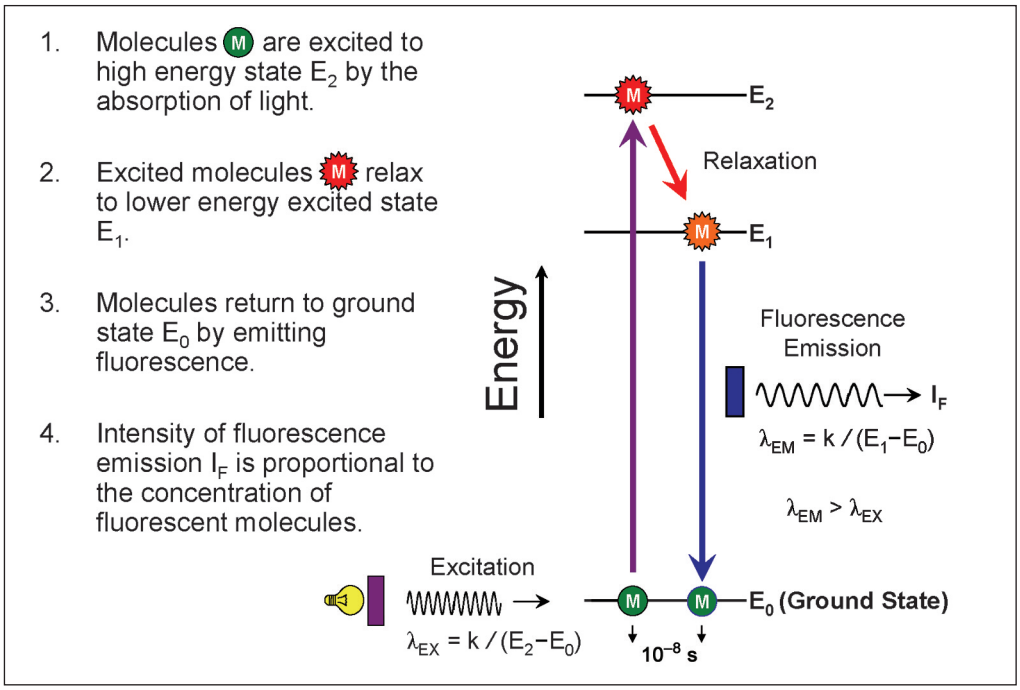


Figure 1:
The fluorescence process.

water, cooling water discharge, or sewer systems. These facilities usually have a permit (National Pollutant Discharge Elimination System, etc.) to allow the discharge of some pollutants. The permits spell out the frequency and method of monitoring and the allowable concentration of the specific pollutants. For petroleum hydrocarbons the monitoring usually entails a 1 L grab sample from the discharge taken periodically and tested using a gravimetric analytical technique such as the EPA 1664 method [1]. The discharge concentration requirements of petroleum hydrocarbons will vary depending on location and whether the discharge is to the local sewer system or to the environment (river, lake or ocean). The concentration can vary between 15 mg · L^{-1} to 200 mg · L^{-1} to zero discharge.

When the EPA 1664 method [1] is used, an accredited laboratory does the testing. The minimum detection limit of the method is stated at 5 mg · L^{-1} liter of hydrocarbons, and the accuracy of the method is about ±20 % of the reported concentration.

Industrial facilities typically have a mechanism to prevent excess petroleum hydrocarbon concentrations from discharging from their facility. These mechanisms can be as simple as a weir in a tank to collect any hydrocarbons or as sophisticated as hydrocyclones, air flotation cells, activated carbon, etc. Usually, the systems are simple, with no or minimal moving parts and rely on resonance time or a droplet-coalescing media to remove the petroleum.

The simple separation systems are designed for a specific wastewater flow rate, specific hydrocarbon concentration range, droplet size, specific gravity of the oil, etc. If conditions in the wastewater are outside the design range of the system, the discharge concentration may exceed the permitted limit. If this happens during the periodic sample event, the facility can be fined by the local authorities. Frequent out-of-compliance events or a serious spill may force the facility to improve or replace their wastewater treatment systems. Further, the facility can be responsible for the cleanup costs of a spill or leak.

Cooling Water

Industrial facilities with large rotating equipment or hydraulic systems will have some form of oil cooling system using air or water. Water is used in either a closed loop with a cooling tower or in an open-loop system where the cooling water is pulled from a local water source and discharged directly back to the water source.

Heat exchangers used to cool the lube and hydraulic oils can leak and, therefore, contaminate the cooling water system. When a closed-loop system is used, the contaminating oil will circulate through the system and increase in concentration, fouling the system and requiring additional water treatment chemicals and their related cost. If the leak is not detected in time, the cooling tower can become fouled and require significant down time for cleaning. Some facilities are required to monitor the air quality around the cooling tower for volatile organic carbons (VOC). Unmonitored oil leaks into the cooling tower can increase VOC discharge to the atmosphere. In open-loop systems a leak can be discharged directly into the envi-

ronment. If the cooling water has a regulated environmental discharge point, the periodic grab sample will eventually show the leak and can result in fines for the facility.

Steam Cycles

Some petroleum hydrocarbons like #6 fuel oil and asphalt require heating with steam to reduce the viscosity and allow the hydrocarbons to flow. Most facilities would prefer to return the steam condensate and recover the heat energy. Boilers, however, have a limit to the hydrocarbon concentration present in the feedwater. If the steam generated is used for power generation, ASME states that the hydrocarbon concentration must be below 1 $mg \cdot L^{-1}$ and lower than 0.25 $mg \cdot L^{-1}$ for high pressure boilers. Because of the potential for leaking heat exchangers, many facilities do not recover the steam condensate used to heat hydrocarbons.

When the steam pressure is dropped through a turbine it is possible for some lube oil to leak through the turbine bearing seals. The lube oil can leak in very small amounts compared to the total volume of lube oil in the system. If the plant monitors the lube oil volume in order to detect leaks, this small volume lost may not be noticed until after the boilers have been damaged.

Solutions

Fluorescence oil-in-water monitors have been used successfully to detect and reduce the number of out-of-compliance discharge events of separation systems and to detect leaking heat exchangers at trace concentrations. Online and grab sample analyzers are used for this purpose. When these monitors are calibrated or correlated to the lab method used to report the petroleum discharge concentration, the plant operators will have quick and reliable information about the performance of their wastewater system. If the system is upset, they can take action to prevent the discharge concentration from exceeding the permitted oil concentration.

Fluorescence oil-in-water monitors are chosen for these installations because of their sensitivity to low concentrations of oil and because of their wide linear measurement range. Low maintenance design and selectable optical configuration are product features that are important for long-term successful installations.

Typically an oil platform in the Gulf of Mexico has a 29 $mg \cdot L^{-1}$ discharge limit. Monthly water samples are collected and analyzed at accredited laboratories using the EPA 1664 gravimetric method to determine the oil content. Data collected from an oil platform in Figure 2 illustrates the results over four days from an online monitor. The data shows that the normal discharge of this platform is about 15 $mg \cdot L^{-1}$, and illustrates that upset conditions are easily detected and the cause identified.

Figure 3 illustrates a wastewater discharge process at an oil refinery as measured by a fluorescence monitor calibrated to show total petroleum hydrocarbons. In the graph, the measurement from the oil-in-water monitor is compared to a turbidity monitor. Turbidity monitors are commonly used as a low cost alternative to fluorescence. The problem is that turbidity or light scatter monitors give false alarms of oil content in the presence of high solids and false negative alarms in the presence of dissolved hydrocarbon droplets that are too small to be detected. Only the fluorescence monitor was able to indicate the dissolved and droplet-sized oils in the presence of solids.

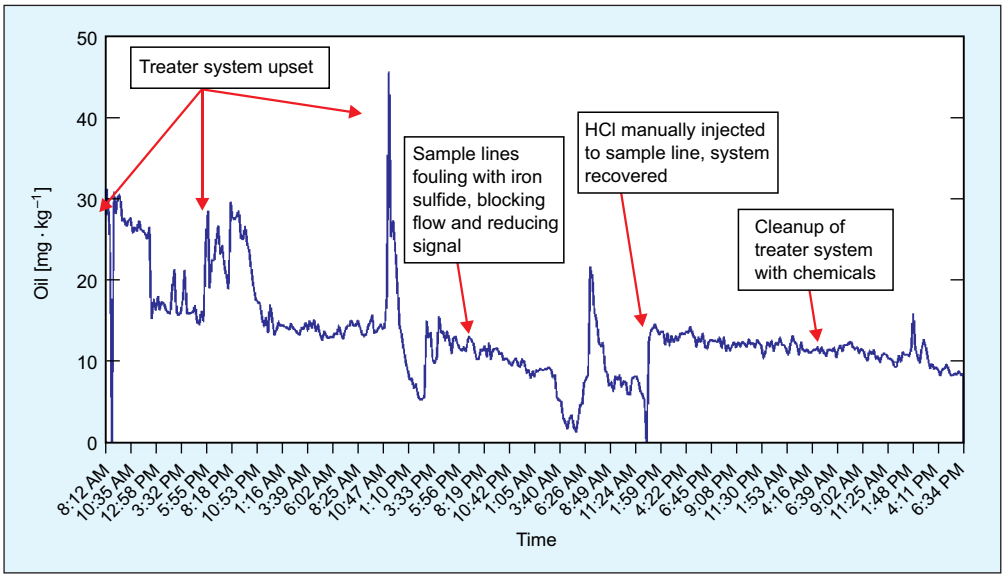


Figure 2:
Offshore oil platform in Gulf of Mexico – oil-in-water monitoring.

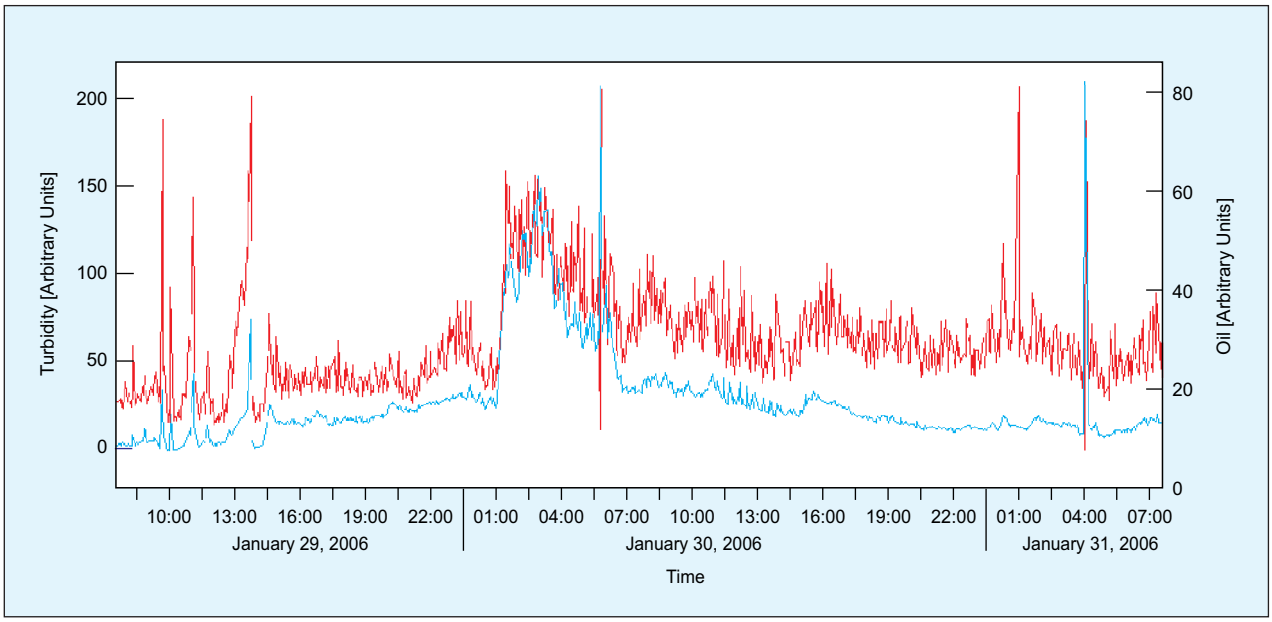


Figure 3:
Water discharge from an oil refinery – turbidity (in red) vs. total petroleum hydrocarbons (in blue).

If high oil content wastewater is detected, it can be recirculated back into the wastewater treatment system for further processing. In many cases, a polishing filter is used to remove most of the petroleum hydrocarbons remaining after the gross separation system (see Figure 4). The oil-in-water monitor gives the plant operators control of the process and the discharge. Polishing filters can be quickly consumed by the continuous absorption of low hydrocarbon concentrations. In this application, the monitor can be used to direct flow to the filters only when needed, thereby saving media replacement costs.



Figure 4:
Online hydrocarbon monitor in a wastewater treatment unit.

Being able to detect lube and hydraulic oils below 2 $mg \cdot L^{-1}$ in cooling water can give the plant operators early warning of a leaking heat exchanger. This can allow the operator to respond quickly and take the heat exchanger out of service for repair before the leak has become catastrophic. The early detection can also reduce the amount of treatment chemicals used and can reduce the cost of repairing the heat exchanger.

Table 1 lists the detection limits of some lube and hydraulic oils in deionized water for the California Environmental Protection Agency certified Turner Designs TD-4100 Online Hydrocarbon Monitor [2].

Figure 5 shows an online oil-in-water monitor protecting a cooling tower.

Protecting boilers from fuel oil in return condensate is a classic application of fluorescence monitors. Fuel oil #6 can be detected at 5 $\mu g \cdot L^{-1}$ in steam condensate. This limit is below the maximum allowable hydrocarbon content in boiler feedwater for high pressure steam boilers. Using fluorescence monitors has allowed plants to be able to recover energy from the steam condensate used to heat heavy hydrocarbons and/or to dump the condensate to protect the boilers.

Figure 6 shows an online monitor in a boiler feedwater analyzer package at a refinery in Salt Lake City, Utah, USA. The analyzer package allows collection of samples for water chemistry analysis.

Oil Grade	Detection Limit [mg · L^{-1}]
Nytro 10XN Lube Oil	0.78
Mobil Gear 600 XP	0.1
Mobil DTE 220	0.1
Mobil DTE Extra Heavy	0.3
Royal Purple ISO 320	0.2
Royal Purple ISO 220	0.3
Royal Purple 46	0.2
Mobil SHC 220	0.6
Mobil DTE 25	0.5
Mobil Gear SHC 220	2
Mobil DTE Heavy Medium	0.034
Mobil DTE 732 Lube Oil	0.41
Mobil DTE 746	0.9
Diesel	0.011
Teresso 46 Lube Oil	0.036
Quaker Ferrocote 61A	0.015
Sullube	1.84
Mobil DTE 24	0.17
Mobil Spartan 460	0.13
Mobil 1 DTE 797 Lube Oil	0.090
Fyrquel	0.009

Table 1:
Turner Designs TD-4100 Online Hydrocarbon Monitor – Detection limits of some lube and hydraulic oils in deionized water.



Figure 5:
Detection of oil-in-water monitor in cooling water.



Figure 6:
Oil-in-water monitor as a part of the feedwater sampling and monitoring rack.

Reliable detection of heat exchanger leaks has allowed some facilities to take an additional step of using lube and hydraulic cooling water as a boiler feedwater makeup source. Because the cooling water is a higher temperature than other water sources, the plant's fuel costs are reduced.

Quick and reliable monitoring for hydrocarbons in wastewater, cooling and heating water is valuable to industrial facilities. With the proper maintenance and application, fluorescence monitors have been effectively used to indicate process upsets and leaks to reduce environmental issues.

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Chip Westaby (B.S., Mechanical Engineering, University of California, San Diego, CA, U.S.A.) has over 14 years of experience in instrumentation and controls. He has been an application engineer, a field engineer, a sales engineer and a regional sales manager for specialized process instrumentation and monitors for oil/water separation and controls. Chip Westaby has presented papers on measurement technology and process optimization at the Produced Water Society, the Instrumentation Society of America, the Southwest Chemistry Workshop, and the Electric Utilities Chemistry Workshop, as well as at other international workshops.

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