Understanding and Monitoring Hydrocarbons in Water

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Introduction

Hydrocarbons are a common and natural occurrence in the environment and varying concentrations in stormwater and effluent water are not unusual. Hydrocarbons in water can be found as free floating, emulsified, dissolved, or adsorbed to suspended solids.

A hydrocarbon, by definition, is one of a group of chemical compounds composed only of hydrogen and carbon. Typically, hydrocarbons are broken down into three main classes; aliphatic, alicyclic, and aromatics. Further sub-classes can also be defined. Simply stated though, hydrocarbons are organic compounds made up of hydrogen and carbon.

Microbes in the soils and water have a natural ability to breakdown many of the these compounds and any hydrocarbon which is exposed to the air will also have an affinity to volatilize. As well, reactions including photochemistry, and the various transformations of the hydrocarbon through these reactions can enhance the hydrocarbon decomposition.

Industrial processes and man induced activities often result in the increased loading of hydrocarbons in water. The natural abilities of the water to decompose the hydrocarbons become overwhelmed and the resulting affect on the environment includes, but is not limited to:

-oils can affect respiration of fish by adhering to the gills

-oils adhere to and destroy algae and plankton

-feeding and reproduction of water life (plant, insect, and fish) is affected

-aesthetics is affected by sheens

-micro-organisms needed for plant nutrition is redirected to oil degradation

Typical sources of man induced hydrocarbons include the refining processes of crude oil into gasoline, lubricating oils, kerosenes, etc.. As well, the resulting commercial products find their way into the environment through stormwater run-off and spills from road asphalts, fueling depots (ie. airports, maintenance facilities), transportation and haulage, cooling water systems, manufacturing facilities such as automotive, plastics and steel production, and wood distillation industries.

Understanding hydrocarbons and the techniques to monitor for them is an important part in the assessment of filters and separators, and the associated productivity and environmental impacts they can have.

Hydrocarbons Defined

As stated simply above, a hydrocarbon is a compound of hydrogen and carbon. Of course, the chemistry involved can be a lot more complicated than this. In fact, there could be over 10,000 individual organic compounds in one sample of conventional or synthetic crude oil. And of these, hundreds could be of a hydrocarbon nature.

There can be many confusing references to hydrocarbon contamination water. Terminology such as……..

PAH's (polycyclic aromatic hydrocarbons)
BTEX (benzene, ethylbenzene, toluene, xylene)
TPH (total petroleum hydrocarbons)
TRPH (total recoverable petroleum hydrocarbons)
TOG (total oil and grease)
Organic vs. **Inorganic**

………all contribute to this confusion.

Generally, hydrocarbon contamination in water is directed to total parts per million (ppm) levels of the hydrocarbon in water. For example, a hydrocarbon level of 30 ppm in water could contain any number of compounds that total this 30 ppm; including compounds found in jet fuels, diesels, lubricating oils, etc.. In other words, the source of the hydrocarbon and the specific compound is not particularly targeted. It is the overall total of hydrocarbon compounds that is typically of interest.

A hydrocarbon can refer to a vast array of compounds, but a determination of a *contaminating* hydrocarbon will help to define this scope. As well, acceptable and available measurement techniques may define a contaminating hydrocarbon even further.

The three main classes of hydrocarbons, described in greater detail, are:

Aliphatics are open chain compounds, bonded in a linear fashion, and are saturated or unsaturated. Saturated (single bond) aliphatics are often referred to as paraffins or alkanes. Unsaturated aliphatics are known as olefins or alkenes (double bond), acetylenes or alkynes (triple bonds), diolefins or alkadienes (two double bonds), and alkatrienes and alkeynes (multiple double or triple bonds). Typical aliphatics include ethane, actelyene, and 1,2-butadiene, and the most popular; methane.

Fig. 1 Aliphatic Compound example: note the linear bond fashion that leaves the molecules open ended. This particular triple bond compound shown is named acetylene.

Alicyclics, as indicated by their name, contain rings of carbon atoms in their structure. The ring size and number can vary which increases the number and classes of this compound. Multiple ring compounds are referred to as polycyclic alicyclic compounds. The saturated alicyclic hydrocarbons are often called napthalenes. Examples of alicyclics include cyclopropane and cyclopentane

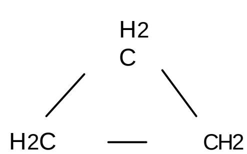

Fig. 2 Alicyclic compound example: note the circular (cyclic) bond fashion that leaves the molecules close ended. This particular compound shown is named cyclopropane.

Aromatics typically contain at least one 6-membered benzine ring in their make-up. Polycyclic aromatic hydrocarbons (PAHs) therefore include multiple ring compounds that include the benzine ring. As the name infers, these compounds typically possess a fragrance. A few aromatic compounds include ethylbenzine, vinylbenzine (styrene), toluene, xylene. The aromatics include what are often referred to as BTEX compounds.

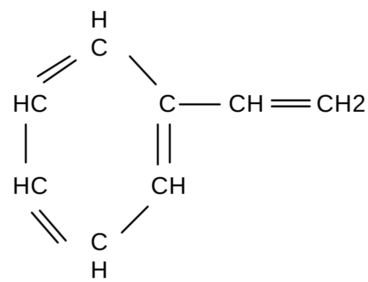

Fig 3. Aromatic compound example: note that a benzine ring (on the left) is in the make up of the compound. This particular compound shown is named vinylbenzene (styrene).

Most unrefined crude oil does not contain high concentrations of aromatic hydrocarbons. The aromatic hydrocarbons are typically the result of the refining process and are produced during the distillation (cracking) operations of a facility. Aromatics are therefore commonly associated with gasoline, jet fuels, diesel, kerosene, lubricating oils, and transformer oils.

As such, the aromatics are typically the target of monitoring instruments to verify distillation efficiency, filtration and separation effectiveness, and environmental contamination.

Regulatory Efforts

Environmental interest groups, government bodies, regulatory agencies, and of course, the general public and private industry itself all have a legitimate concern with regards to hydrocarbons in water.

On a global perspective, agencies such as the International Maritime Organization and the World Health Organization, have an interest in the overall quality of water, especially since water contaminants and their resulting affects do not respect international borders. Various international conventions have enacted regulations with regards to hydrocarbon contamination in water.

On a national scale the Environmental Protection Agency (USEPA) and the American Petroleum Institute (API) in the United States, Environment Canada, and the Ministry of Water Resources in China are examples of government and private bodies that are active in the participation and support of standards and methods of monitoring hydrocarbons in water. Within the world, any number of countries or groups of countries could have monitoring initiatives in place that are independent of international policies.

At state, provincial, and municipal levels of government, issues regarding water contamination are also evident. It becomes obvious at the municipal infrastructure level that a local water treatment facility would not want to be burdened with abnormally high levels of hydrocarbons in water that could upset normal treatment operations for drinking and recreation waters.

When water is used by, or comes in contact with a private or public activity, it is the responsibility of that activity to ensure that any hydrocarbon levels in the water effluent are within the guidelines determined for the recipient use. Use caution, there may be several jurisdictions with interests in one specific point of contamination.

Review of Monitoring techniques

There are a few different techniques available to determine hydrocarbon levels in water. Technologies that are restricted to laboratory use may provide the most valuable data, but are not favorable to field use where fast reading times are critical for the management of an effective processing and effluent operation.

For contamination purposes, the USEPA determined that hydrocarbon extractables could provide a basis to the measurement of ppm levels of hydrocarbons in water (EPA Method 413.1).

Originally freon was used to extract the hydrocarbons from the water. Once extracted, these could be quantitatively analyzed to provide an indicator of the ppm (or mg/l) of hydrocarbon in water. Atmospheric ozone depletion through the use of freons is changing this method towards the use of hexane (EPA Method 1664). This method readily provides the user with a hydrocarbon sample in the field. Basically, this approach suggests that if a hydrocarbon can be extracted from water, it can, and should be, monitored.

This technique provides data from a sample drawn at a specific time. It does not provide a continuous, real-time indication of the hydrocarbon levels in a continuously operating process stream.

Generally, measurement techniques can be categorized as discrete sample or continuous on-line devices. Typical approaches to monitoring include:

- Gravimetric (weight)
- Colorimetric
- Infrared
- UV Absorption
- Nephelometry
- Fluorescence

Gravimetric: This technique of hydrocarbon determination is described under the EPA Method 413.1 which uses an extraction additive. Freon-113 is added to a water sample and a subsequent boiling off of the water and Freon leaves the oil and grease which can then be weighed. EPA Method 1664 uses n-hexane to extract the oil and grease to be weighed. This method allows the total oil and grease to be measured in mg/l. A sample must be drawn from the process and taken to a lab to perform the procedures. This is not conducive to field use because of the equipment necessary.

Colorimetric: This can be a direct scan measurement of the sample or can use a technique similar to gravimetric in that an extraction takes place. A catalyst is then added to the extracted mix which initiates a dramatic color transformation.

The resulting color can be compared to a color chart or analysed using a spectrophotomer.

This method provides a more direct approach than weighing which makes it more practical in the field. However, a data base of standards of colours must be collected for each different hydrocarbon and application. For example, a water test and resulting colour will not provide the user with a ppm level of hydrocarbons directly. The user must know what general type of hydrocarbon is in the water (ie. transformer oil) and then compare the colour to a Transformer Oil chart that has been previously documented. Portable, laboratory, and field colorimeters are available that will analyze the colour and compare it to a data bank.

Infrared: Historically, this has been a widely used method of measuring for hydrocarbons in water. This technique looks at the total number of hydrogen and carbon bonds and, through a pre-determined calibration input, provides a ppm indication of the total hydorcarbons.

Typical units are transportable and require a discrete sample input. On-line devices are also in practice that will provide a near continuous indication of hydrocarbons.

Infrared employs the use of energy absorption. Hydrocarbons absorb energy at a specific wavelength (3.4 micrometers) and the amount of energy absorbed is proportional to the amount of hydrocarbons. Since other materials also absorb energy in this range (including water), the oil must first be removed from the interfering background. An extraction, as described above is typically used for discrete samples.

On-line devices usually incorporate a submersed and specially coated fiber cable that draws the hydrocarbons from the water and onto the fiber for analysis. The fiber is then mechanically cleaned off prior to the next reading.

UV Absorption/Transmission: This is similar in approach to the infrared, however the hydrocarbons do not need to be extracted from the water. This makes the unit applicable to laboratory and on-line applications. Different compounds absorb UV light at different wavelengths. By emitting UV light at a specific wavelength into the water, the hydrocarbon level can be determined by measuring the amount of light absorbed (the inverse of the amount that is transmitted through).

While this technique is quite selective to hydrocarbons, there are organics such as bacteria and algae, as well as suspended particles, that will interfere with the the light transmission (and hence, absorption) measurement. Compensation, filtering, or frequent zeroing is therefore required in many applications.

Nephelometry: Also referred to as light scattering, this technique uses light intensity measurements through the water to indicate ppm levels of oil in water.

Oil in water can cause the light to refract (scatter) in a predictable manner that can be monitored. An increase in oil content causes a light intensity decrease directly across from the emitter and a light increase can be measured at a point of scatter. Measurements can be done at either point.

This technique provides a cost effective in-line measurement. The sample must be stable with regards to any other sources of interference to the light path. These can include suspended solids, other chemical compounds, and color additives that may cause the light to scatter and result in a false hydrocarbon reading. Compensation and filtering techniques are often used to offset any possible interference.

Fluorescence: This technique also uses a UV light source, however, the actual absorption is not measured but rather, the fluorescing characteristics of specific compounds is monitored.

Fluorescence is a phenomenon whereby a portion of the absorbed wavelength in the targetted compound is re-emitted at a higher wavelength. When the water is excited at a specific wavelength of UV light, certain compounds, including hydrocarbons, will absorb energy. Even fewer compounds will re-emit this light at a higher wavelength. Hydrocarbon compounds will re-emit at a wavelength range that is unique to them. By measuring the fluorescence intensity at this wavelength, the ppm level of hydrocarbons can be determined. This approach makes the instrument very selective to hydrocarbons.

For benchtop units, an extraction of oil from the water can be used to provide accurate results to regulatory standards. Straight water samples can be inserted, making the unit an ideal screening tool to determine that hydrocarbons are present.

Fluoresence is available in laboratory and on-line instruments. Compensation and sample conditioning for background interferences is not typically used with on-line instruments. This allows continuous and instantaneous readings without consumables.

Other techniques: Radar, Microwave, Acoustic, and Capacitance are a few alternative technologies used in the oil/water industry, however, these are typically restricted to per cent levels (not ppm) of hydrocarbon content in water or are more suited to separated hydrocarbons such as slicks on bodies of water.

The Fluorescence Approach On-line

One of the favorable characteristics of fluorescence is that the UV source and the receiving monitor do not need to be in direct contact with the liquid.

A common concern in field instruments is the routine maintenance and cleaning of wetted components. In fluorescence, the UV lamp can hover in front of or above a passing sample and not actually touch it. Also, since fluorescence looks for light re-emitted from the hydrocarbon compounds, the hydrocarbons themselves will send the light back out of the water so it can be detected by another hovering (non-contacting) sensor.

For non-contacting systems, the instrument cannot return the water to the process under the incoming process pressure. The passing water must outfall to drain or be collected and returned to the process by pump or other discrete method.

The sensor response to hydrocarbons in water is continuous and instantaneous allowing operators to maintain ppm data over periods of time as well as interlock to controls for real-time response to changing or upset conditions.

Designs can be very simple and direct or include scanning optical devices to increase the selectivity to specific compounds.

The design approach of the fluorescence manufacturer will result in the resolution and praticality of the instrument.

A wide and open shallow stream provides a stable viewing area for a sensor. Suspended solids interference is negligable using this wide path approach due to the area vs. water depth ratio.

A thick free falling tube of water with a concentrated light source and receiver may offer a lower range but suspended solids and fluctuating water conditions can be more of an influence.

Summary

While the definition of an actual hydrocarbon may be quite clear, the definition of a hydrocarbon condition or contamination in water is not as clear.

The type of hydrocarbon and the ability to reliably monitor for it within practical means plays an important role in this definition.

Measurements should be made within an industry standard to provide a common ground for comparison and discussion. However, each individual user will need to determine the technique that is best suited to their specific application.

The decision may in fact, be a combination of units. For example, a fluorescence on-line may be best for continuous use and process monitoring, but a calibration and routine check against a benchtop extraction would provide complimentary and verification data. For regulatory requirements, gravimetric measurements may also be necessary on a determined frequency.

Easily accessible parts for any cleaning is a prerequisite. And of course, inexpensive and field replaceable consumables are also important.

For field instrument use, simple is typically better. A comfort level is required between the operator and the instrument. Without this, the unit will not be maintained properly and the data will be questionable.

Reference material available on request.

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