ABSTRACT
Heat exchanger hydrocarbon leaks into refinery cooling towers have long been the cause of corrosion, fouling, and loss of heat transfer due the presence of the hydrocarbon itself and the resulting increased microbiological growth. Typical methods to control microbiological growth in the presence of hydrocarbons include the use of oxidizing and nonoxidizing biocides. Excessive use of these materials can cause additional corrosion and/or be prohibitively expensive. Common methods of checking exchanger inlets and outlets for hydrocarbon or oxidant residual are often unable to pinpoint the leaking exchanger. The paper details two methods by which light and heavy hydrocarbons may be positively identified by using either activated carbon or a gas trap followed by gas chromatography. Once the leaking hydrocarbon is positively identified, the task of finding the leaking exchanger is simplified dramatically.

INTRODUCTION
Hydrocarbon leaks in cooling water systems significantly and adversely affect equipment performance and operating costs. Therefore, quick determination of the source of the hydrocarbon leak is required. Unfortunately, the process of determining the source of hydrocarbon leaks in cooling systems can be long (several months) and tedious. Any efforts to improve the simplicity of this process and reduce the overall time will have a bottom line effect on plant performance and operating profits.

WHY HYDROCARBON LEAKS ARE BAD FOR COOLING WATER SYSTEMS

Hydrocarbon Leaks Cause Microbiological Growth in Cooling Water Systems
Open recirculating cooling water systems provide an excellent environment for the abundant growth of microbiological organisms.

This microbial growth will lead to the formation of biofilms on system metallurgy which can cause significant loss of heat transfer, promote metal corrosion, and accelerate deterioration of cooling tower internals.

A hydrocarbon process leak in a cooling tower acts as a food source for the naturally existing microbiological life forms (algae, fungi, and bacteria) present in the cooling tower, pipes, and exchangers. In many ways the cooling tower may be compared to a microbiological waste treatment plant. Many waste treatment plants utilize microbiological activity to "eat" the hydrocarbons and other pollutants in the wastewater streams. Chevron El Segundo has a microbiological waste treatment plant (activated sludge) that cleans up the refinery's wastewater before discharging to the Santa Monica Bay. The process conditions of a cooling tower and those of a microbiological waste treatment plant are very similar. Both water systems operate at a temperature between 70°F and 100°F with an oxygen-rich environment. Given any process contaminants, microbiological activity will increase. Unfortunately, in a cooling tower this microbiological activity is detrimental to the successful treatment and protection of the system metallurgy.

A process leak in a cooling tower can promote the growth of both aerobic and anaerobic bacteria in a cooling water system. Aerobic bacteria thrive in oxygenated waters and anaerobic bacteria are inhibited or killed by oxygen. Both forms of bacteria are present in cooling water systems, and their growth is increased by the presence of hydrocarbons.

Table 1 summarizes the microbiological (MB) activity growth potential for various levels of hydrocarbon contamination in a cooling water system.

<table>
<thead>
<tr>
<th>Contamination Level</th>
<th>Sessile Count, CFU/cm²</th>
<th>Planktonic Count, CFU/mL</th>
<th>Time for MB counts to double, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>&lt;10⁶</td>
<td>&lt;10⁴</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>Moderate</td>
<td>10⁶ - 10⁷</td>
<td>10⁴ - 10⁶</td>
<td>3 - 10</td>
</tr>
<tr>
<td>Severe</td>
<td>&gt;10⁷</td>
<td>&gt;10⁶</td>
<td>&lt; 3</td>
</tr>
</tbody>
</table>
During a severe hydrocarbon leak, the microbiological populations can double every three hours in an open recirculating cooling system if not properly treated.

The main effect of microbiological growth in cooling water systems is fouling. This microbiological fouling can quickly reduce heat exchanger and equipment performance and lead to rapid corrosion of metal surfaces. Microbiologically influenced corrosion (MIC) occurs through three methods: physical deposition, production of corrosive byproducts, and depolarization of the corrosion cell caused by chemical reactions.1

First, the nature of biofilms (physical deposition) prevents corrosion inhibitors from reaching and passivating the fouled surface. Second, the byproducts of the biofilm are corrosive and include organic acids and hydrogen sulfide. These byproducts concentrate within and under the biofilm, causing metal corrosion. Finally, corrosion tends to be self-limiting due to the buildup of corrosion reaction products. However, microbiological organisms will absorb some of these materials in their normal metabolism, removing them from the corrosion site. The removal of these reaction products, termed “depolarization,” will stimulate further corrosion.

In addition, as previously mentioned, the presence of a biofilm will severely reduce the performance of heat exchangers by limiting heat transfer. Biofilms are 25 to 600 times more resistant to conductive heat transfer than many metals.2

The presence of hydrocarbons in open recirculating cooling water systems will stimulate the growth of microbiological organisms. Unless properly controlled, through the proper application of nonoxidizing and oxidizing biocides, this microbiological activity will cause fouling and corrosion within the cooling system.

Second, in many cases increased amounts of chlorine (bleach and gaseous chlorine) are fed to control and minimize the increased microbiological activity. These large increases in the chloride ion concentration of the cooling water increase the corrosion potential. High chlorine feed can be destructive to the program chemistry and affect corrosion protection. In addition, the chlorine is aggressive to “yellow” metallurgy (admiralty, brass, copper) and increases corrosion of these metals.

Table 2 summarizes the effects a hydrocarbon leak may have on cooling water system corrosion.

### Table 2: Effect of Hydrocarbon Contamination on Cooling System Corrosion Rates

<table>
<thead>
<tr>
<th>Contamination</th>
<th>None</th>
<th>Moderate</th>
<th>Severe</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS general corrosion rate, mpy</td>
<td>1 - 3</td>
<td>5 - 20</td>
<td>&gt; 20</td>
</tr>
<tr>
<td>ADM general corrosion rate, mpy</td>
<td>0.1 - 0.3</td>
<td>0.5 - 1.0</td>
<td>&gt; 1.0</td>
</tr>
<tr>
<td>“Sweet” leak (no H₂S)</td>
<td>0.1 - 2.0</td>
<td>2.0 - 4.0</td>
<td>&gt; 4.0</td>
</tr>
<tr>
<td>“Sour leak” (H₂S)</td>
<td>0.1 - 2.0</td>
<td>2.0 - 4.0</td>
<td>&gt; 4.0</td>
</tr>
</tbody>
</table>

**Hydrocarbon Leaks Cause Fouling in Cooling Water Systems**

Hydrocarbon contamination of cooling water systems can act to foul the system through several methods. Each of these methods act to reduce heat exchanger and equipment performance through loss of heat transfer and reduced cooling water flow rates.

First of all, significant buildup of the hydrocarbon itself can cause the fouling. Many oils and heavy hydrocarbons will build up on pipe walls and exchanger surfaces. At the higher temperatures observed on exchanger tube walls, these hydrocarbon deposits can accumulate quickly and be extremely difficult to remove. There are some surfactants available that will help to inhibit the hydrocarbon fouling but few will eliminate the fouling, especially in severe cases of contamination.

Second, the hydrocarbon may act to bind suspended matter. This new “hydrocarbon-bound” material is difficult to keep suspended and will deposit on tube surfaces and low flow areas. The hydrocarbon may also interfere with the cooling water dispersant and reduce the ability to minimize typical deposits of calcium and phosphate salts. Therefore, inorganic deposits may also result from hydrocarbon contamination.

**Hydrocarbon Leaks Cause Increased Corrosion in Cooling Water Systems**

In addition to microbiologically influenced corrosion, a hydrocarbon leak also causes corrosion in cooling systems by two other major methods.

First, the hydrocarbon can buildup and form deposits on the metal surfaces. This deposit formation will act to prevent cooling water corrosion inhibitors from reaching and passivating the fouled surfaces.
Hydrocarbon Leaks Result in Increased Plant Operating Costs

Plant operating costs will be increased with hydrocarbon leaks due to increased equipment maintenance, reduced plant throughput, increased water usage, and increased chemical costs.

In most cases, the presence of hydrocarbon will increase equipment maintenance costs for several reasons. First, due to the many forms of fouling associated with a hydrocarbon leak, equipment cleaning costs increase. During a plant shutdown, exchangers must be pulled out of service and the fouling cleaned from tube surfaces.

In addition, the cooling tower may need to be cleaned. The tower distribution deck should be vacuumed due to heavy accumulation of hydrocarbon or microbiological growth. The tower internals will need to be cleaned, especially if film-type fill. If the fouling is heavy enough, the film-type fill support structure will not be able to support the increased weight and the cooling tower internals may collapse. The tower basin may need to be emptied to clean and remove any sludge buildup. This sludge may consist of hydrocarbon, microbiological mass, and suspended solids which have deposited.

As a result of hydrocarbon contamination of the cooling system, several critical exchangers may become fouled and the plant throughput may be limited due to a reduction in heat transfer (reduced cooling capacity). Unless additional cooling capacity is available or these exchangers can be quickly removed and cleaned, the plant throughput will be adversely affected.

Plant throughput may also be reduced because of environmental or safety concerns. If the level of the hydrocarbon contaminant in the cooling water system is high enough, discharge restrictions may apply to the cooling tower blowdown. In addition, these high levels of hydrocarbon may pose health or safety risks with the cooling tower operation. Explosivity of the cooling water and cooling tower exhaust should be regularly checked using an approved LEL meter. If a cooling water discharge limit applies or the hydrocarbon concentration is great enough to create the potential for an explosion, plant throughput will be reduced.

In order to minimize the hydrocarbon concentration in the recirculating cooling water, cooling tower blowdown is usually increased. This will minimize the fouling associated with the hydrocarbon contamination.

Obviously, this increases the cost of the plant operation by increasing purchased water and discharge water costs. A common estimate for water is $1.00 for every 1000 gallons purchased and a minimum of $2.00 for every 1000 gallons discharged. This is equivalent to $30,000/yr for every 20 gpm increase in blowdown.

Finally, the chemical treatment costs must increase to properly treat the system during hydrocarbon contamination upsets. In most cases, this chemical treatment is focused on minimizing the effects of the hydrocarbon contamination, not eliminating them. The corrosion inhibitor must be increased to minimize the increased corrosion rates. The cooling water dispersant must be increased to offset any interaction with the hydrocarbon and provide adequate scale inhibition. A microbiological and/or hydrocarbon surfactant should be fed to minimize hydrocarbon and microbiological fouling. Finally, increased biocide usage is required to maintain microbiological control. In many cases, a nonoxidizing biocide is fed because it is technically impractical to feed the high amounts of oxidizing biocide (bleach, bromine, chlorine gas). High amounts of oxidizing biocide may increase metallurgy corrosion and may be ineffective due to the reaction between the oxidizer and the hydrocarbon. Therefore, nonoxidizing biocides are normally fed to control MB growth. These nonoxidizing biocides are much more expensive than regular oxidizing biocide applications. Overall chemical treatment costs may increase 20 to 100% during a hydrocarbon contamination upset of a cooling water system.

Hydrocarbon leaks in cooling water systems significantly and adversely affect equipment performance and operating costs. Therefore, quick determination of the source of the hydrocarbon leak is required. Unfortunately, the process of determining the source of hydrocarbon leaks in cooling systems can be long (several months) and tedious. Any efforts to improve the simplicity of this process and reduce the overall time will have a bottom line effect on plant performance and operating profits.

Using Common Techniques, It’s Hard to Find a Leak

The most time-honored method of finding a hydrocarbon leak in a refinery is to sample the heat exchangers inlet and outlet water and try to determine, either visually, or with a field test or lab tests, which exchanger is leaking.
Using analytical tests, it is sometimes possible to detect the leaking exchanger by a direct oil and grease measurement which may be gravimetric or based on the infrared absorption of an extracted sample. Other tests include oxidant residual testing or Chemical Oxidant Demand (COD). Additional methods include testing for “tell-tale” contaminants, such as sulfide, ammonia, or phenol.

While valuable tools, the above-mentioned techniques are frequently ineffective. Often exchangers do not have taps on both the inlet and outlet to permit individual sampling. Also, the search for “tell-tale” contaminants is hampered by the presence of these target compounds in more than one of the process streams. The oxidant residual testing can be rendered ineffective, either by having a compound that is slow to react or by having lost all oxidant residual due to the leak itself.

Direct tests for hydrocarbons, using infrared or gravimetric methods, are the most definitive but are also the most labor intensive. Because of their complexity, it is best to minimize the number of samples. It is often thought that by only sampling at major tie-in points in the cooling tower supply and return water headers, one can locate the offending plant or complex, thereby significantly reducing the sample load.

The high recirculation rate in most cooling water systems causes process contaminants to be uniformly spread throughout the cooling water system almost instantly. In Figure 1, we have a simplified schematic of one of the towers at the Chevron El Segundo refinery. With 1000 gpm of makeup water, 800 gpm evaporation, and 200 gpm blowdown, the tower is at 5 cycles of concentration. Assuming a hydrocarbon leak has reached equilibrium at 100 ppm HC in the tower, the leak rate must be equal to the loss into the blowdown.

\[
\frac{100 \text{ parts HC}}{10^6} \times \frac{200 \text{ gal}}{\text{minute}} \times \frac{8.34 \text{ lb}}{\text{gallon}} = 0.167 \text{ lb of HC per minute}
\]

The recirculation rate for this tower is 40,000 gpm. For demonstration purposes, we will assume that its flow is routed equally in parallel to ten separate plants. Therefore, the flow rate to each plant will be 4,000 gpm or 33,360 lb per minute. The HC concentration difference for the water leaving the plant with the HC leak will be:

\[
\frac{0.167 \text{ lb of HC}}{33,360 \text{ lb, of water}} = 5.01 \text{ ppm HC in water}
\]

When the plant responsible for the leak is found, the inlet water concentration of HC will be 100 ppm and the outlet water will contain 105 ppm. Unfortunately, the hydrocarbon tests frequently have more variability than 5 ppm, due to a number of factors.

**NEW METHODS**

**Fingerprint**

Within the refinery setting, it’s common to have a library of hydrocarbon gas chromatograms which can be used to identify the various HC streams. The gas chromatograph used at Chevron is a Hewlett Packard 5880 with a flame ionization detector. These GC traces are often referred to as “fingerprints.” They can be used to identify the boiling range of an unknown HC stream to place it within a particular product category, such as gasoline, jet, diesel, gas oil, and the like. With higher resolution, the GC traces can also differentiate within a particular product category, such as the gasoline streams of hydrobate, reformate, alkylate, FCC gasoline, and others. In the latter case, the term “fingerprint” is particularly appropriate because it is only by a careful comparison of the chromatograms and a matching of the “peaks and valleys” that a positive identification can be made.

This method can be used for fairly massive HC leaks in cooling towers where free HC can be collected from the tower basin. In this scenario, the HC can be identified by more casual techniques such as, color, odor, viscosity, and volatility.
Referring back to our 100 ppm leak, the problem is getting enough oil for the lab to work with. To that end, we have developed three different concentration methods which have the ability to collect enough HC so that a positive fingerprint identification of the oil can be performed.

**Solvent Extraction**

Our first attempt to concentrate the HC from a cooling water stream involved an extremely simple solvent extraction method. At each cooling tower there is a small lab where the water chemistry tests are run. In the sink, we placed a 1000 mL graduated cylinder filled with roughly 600 mL of trichlorotrifluoroethane (Freon 113.) A piece of tubing was routed from the return water line to the bottom of the graduate. Approximately 1/2 gpm of return water was percolated through the solvent. The solvent which is heavier than water and liquid at room temperature was contacted in this manner for a day or two with additional solvent added to make up for evaporation. Toward the end of the test, the solvent is allowed to evaporate down to roughly 100 mL. This process can achieve a concentration ratio of about 50,000 to one. The HC-laden solvent is then fingerprinted in the lab. With this method, there is easily enough sample to get a positive identification. While convenient, this method had some drawbacks, not the least of which was the prodigious use of chlorofluorocarbons. Consequently, this method was abandoned in favor of an even simpler and more versatile method.

**Activated Carbon Filter**

Activated carbon has the ability to adsorb a wide spectrum of hydrocarbons. When loaded into a flow-through container, it can achieve the same sort of extraction as a solvent. For our purposes, we made up several samplers based on the “sample bomb” motif. We used a 6-inch piece of 3/4” mild steel pipe fitted with reducers and valves at each end. Into this “pipe bomb” we placed granular activated carbon.

When a leak is suspected in one of the cooling towers, one of these activated carbon filled samplers is attached to a return water stream for 1 to 3 days. The flow rate through the sampler is set at approximately one gpm. At the end of this time, the sampler is removed and the carbon is extracted with carbon disulfide which is then injected in the fingerprint gas chromatograph.

These activated carbon detectors have proven themselves at the El Segundo Refinery and we have even been able to offer this service to some of the other Chevron refineries. There is one limitation which had to be addressed — the adsorptive ability of the carbon drops off as the HC gets lighter. In instances where the HC is butanes or lighter, a gas trap is utilized.

**Gas Traps**

The gas trap is simply a 5-gallon plastic carboy with a three-hole threaded cap (available from Cole-Parmer) as shown in Figure 3. One of the holes is designated as the sample point (#1). This sample hole is fitted with a short piece of plastic tubing connected to a 50-mL plastic syringe or Kevlar sample bag. The tubing between the sample syringe/bag and 5-gallon bottle is clamped shut. The outlet hole (#2) is fitted with a piece of plastic tubing which extends to the bottom of the carboy. The inlet hole (#3) is left flush with the bottom of the cap.

To use the gas trap, the bottle is placed near a return water sample point and filled with water. The cap is installed and cooling water is routed into the top of the jug. Preferably this cooling water is sampled from the top of a cooling water return line. Because the water can only escape through the dip tube on the bottom, any gas entering the bottle is trapped at the top. When sufficient gas is in the bottle to fill the sample syringe or bag, the clamp is removed and the sample taken.

The sample is run on the chromatograph which analyzes the fuel gas samples. In addition to the expected oxygen and nitrogen, the gaseous HC is easily detected and identified. This method has the further advantage of being able to pinpoint the leaking exchanger.

![Figure 3: Gas Trap Bottle Apparatus](image-url)