Utilizing TPH GRO, DRO and ORO Effectively and Understanding Overlap of these Ranges

The acronyms TPH GRO, TPH DRO and TPH ORO stand for total petroleum hydrocarbons in the gasoline range, diesel range and oil range respectively. It is important to recognize that these tests are not tests for gasoline, diesel fuel or oil specifically, but rather petroleum hydrocarbons that are in the “range” of those found in gasoline, diesel fuel or oil.

TPH GRO, quantitates petroleum hydrocarbons that are purged from the sample using an inert gas. The inert gas used for purging is normally helium or nitrogen. This gas is bubbled through the sample to drive the volatile hydrocarbons out of the sample. The volatile hydrocarbons are collected on a sorbent trap, desorbed and sent to the gas chromatograph where they are quantitated. TPH GRO is in reality, an analysis for “purgable” petroleum hydrocarbons in the volatile range between C6 and C10. Figure 1 shows the auto sampler that is used to purge the samples with an inert gas.

TPH DRO quantitates petroleum hydrocarbons that are extracted from the sample utilizing a solvent. The solvent used is methylene chloride. The methylene chloride “washes” the petroleum hydrocarbons out of the sample. The solvent is concentrated by evaporation to achieve lower detection limits and analyzed on gas chromatograph where the extracted petroleum hydrocarbons are quantitated. TPH DRO is in reality, an analysis for “extractable” petroleum hydrocarbons in the semi-volatile range between C10 and C28. Figure 2 shows samples in the solvent use to “wash” the petroleum hydrocarbons out of the sample. Figure 3 shows sample extracts that have been concentrated and are ready to go on the instrument for analysis. Figure 3 goes below here and to the right

A sample travels through a specially coated column in the instrument where individual compounds can be separated and displayed on the chromatogram in the order they exit the column (retention time). The height of the individual peaks or area under the mass of peaks (response) allows us to quantify the amount of petroleum hydrocarbons in the sample. Figure 4 shows the column inside a Gas Chromatograph. This particulars column is a 30 meter column, which means the sample travels almost a third football field in distance.
through the instrument.

Figure 3

Figure 5 below is a chromatogram of a diesel standard. On the X axis is retention time, on the Y axis is the detector response.

Figure 5

With this basic understanding of what the TPH GRO and DRO tests actually represent, let’s take a look at a few scenarios. The first is the situation where the TPH GRO has yielded results for a sample collected from a known diesel fuel spill. Whereas the TPH DRO is the appropriate test to utilize for a diesel or #2 fuel oil spills (#2 fuel oil has a composition similar to diesel fuel), it is a common practice to additionally collect a sample for TPH GRO analysis.

Diesel/ #2 fuel oil is largely composed of semi-volatile compounds. There are however a number of volatile compounds, most of which are lost in the TPH DRO extraction process. The odor you detect from a fresh fuel oil spill is largely the volatile components. What we are actually seeing is the lighter end of the diesel/ #2
fuel oil pattern near the end of the TPH GRO run.

The same type of scenario can take place in the TPH DRO analysis when the contaminates are actually #4 and #6 fuel oil. In this situation, we are seeing the lighter end of the #4 or #6 fuel oil late in the TPH DRO run. Figure 6 illustrates how most of a #4 fuel oil exist in the diesel range. The yellow and purple arrows serve as a reference for range utilized for the quantitation of “diesel range organics” (TPH DRO). The yellow arrow delineates the beginning of TPH DRO quantitation (C10) and the purple arrow delineates the end of the quantitation (C28).

Figure 6

A similar scenario can take place with a TPH DRO analysis of a sample that is heavily contaminated with gasoline. In this situation, the heavier end of the gasoline pattern is exhibiting itself at the start of the TPH DRO run. Figure 7 compares chromatogram for a gasoline and diesel fuel standard that were analyzed utilizing the TPH DRO instrument with the yellow arrow representing C10 and the purple arrow C28. The purple arrow in the gasoline chromatogram is purposefully off the page as the analytical run was cut off before C28.
For extractable hydrocarbons, it should be noted that for different fuel weight, there is an optimal analytical run profile and appropriate standards that should be utilized to allow quantitation based on a specific fuel range. This is necessary to provide the accurate analytical results. It is not possible to provide the optimal conditions for every fuel range in a single analysis. Consequently, if #4 or #6 oil is suspected, it would be best to utilize a modification of the TPH DRO analysis we call TPH ORO, where ORO stands of “Oil Range Organics”. With this modification, we are lengthening the TPH DRO run time to see heavier hydrocarbons beyond diesel/#2 fuel, utilizing the appropriate standards and modifying the gas chromatograph analytical run profile for these fuels. When contamination heavier that diesel/#2 fuel is suspected, a discussion with your PSS project manager and comment in the remarks section of the chain of custody form and will ensure we select the most appropriate test(s).

Another example of fuels where the TPH GRO and DRO methods overlap occurs is kerosene and the lighter aviation types such as Jet A. In this case the TPH GRO analysis is normally the best choice unless the fuel in the samples is highly weathered. In which case the TPH DRO analysis may prove useful. Many states regulatory agencies are now requiring that both TPH GRO and TPH DRO analyses be performed on sites contaminated by diesel/#2 fuel, kerosene and lighter aviation fuels. With kerosene and lighter aviation fuels, the quantitative results of the DRO and GRO cannot be added together due to overlap of hydrocarbon detection between the methods.
Figure 8 indicates the overlap in petroleum hydrocarbons in terms of carbon number between the various fuel types.