DRO, EPH, ETPH, GRO, PRO, PVOC, STARS, TPH, VPH? Help, I’m Trapped in Alphabet Soup!

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Introduction

The analysis of samples resulting from fuel and oil spills is different from the analyses routinely performed by either a petroleum or an environmental testing laboratory.

- Many petroleum methods require identification and quantitation using pattern recognition against known reference fuel/oil standards. This is possible when the fuel/oil is relatively pure (such as when contained/protected in a drum or tank).
- Most environmental methods require individual analytes to be identified and quantified. The complex nature of many fuels/oil tends to mask the detection of individual analytes at low levels.

Once a fuel/oil is released into the environment, two factors may contribute to a decrease in its integrity:

1. If more than one fuel/oil type is present, it may be impossible to use pattern recognition because the analyte ratios may not match any reference fuel/oil standards.
2. As the fuel/oil is weathered (evaporation of lower molecular weight compounds and/or degradation from UV rays or oxygen of some or all of the compounds), it becomes very hard to identify fuel/oil type because the analyte ratios may no longer match reference fuel/oil standards. Also, the quantitation of weathered patterns in the samples to non-weathered reference standards is inaccurate.

For soil and water samples collected due to off-shore oil spills, leaking railroad tanker cars and highway tanker trucks after accidents, and underground storage tank (UST) remediation at service stations, it may be preferred to measure contamination by carbon range, instead of by fuel/oil type or individual analytes. The United States Environmental Protection Agency (US EPA), United States Coast Guard (USCG), American Society for Testing and Materials (ASTM), and several States have published methodologies for these purposes.

Terms and Definitions

Several terms associated with the sampling and analyses of environmental samples for fuels/oils are currently used. Because there are many agencies with methods, there are many terms, resulting in ‘alphabet soup’ due to the vast number of acronyms. Also note that the same term may be used by multiple agencies but with slightly different meanings. While not inclusive, Table 1 represents an attempt to define some of the most common acronyms. While there are many methods, they can be grouped into three categories:

- Gasoline Range Organics (GRO): The GRO-like methods are for volatile analytes, and require purge and trap or direct injection
- Diesel Range Organics (DRO): The DRO-like methods are for semivolatile analytes, and require solvent extraction
- Total Petroleum Hydrocarbons (TPH): The TPH methods are for the heavier volatile, the semivolatile, and some heavier analytes, and require solvent extraction

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### Table 1. Terms and Definitions (see References 1-12 n-Alkane)

<table>
<thead>
<tr>
<th>Term</th>
<th>Agency</th>
<th>n-Alkane Range</th>
<th>Aromatic Range</th>
<th>Boiling Point Range</th>
<th>Sample Preparation</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>DRO (Diesel Range Organics)</td>
<td>US EPA</td>
<td>C10-C28</td>
<td>n/a</td>
<td>170-430 °C</td>
<td>solvent extraction</td>
<td>GC-FID</td>
</tr>
<tr>
<td>Alaska</td>
<td></td>
<td></td>
<td>n/a</td>
<td>170-400 °C</td>
<td>solvent extraction</td>
<td>GC-FID</td>
</tr>
<tr>
<td>Wisconsin</td>
<td></td>
<td>C10-C28</td>
<td>n/a</td>
<td>170-430 °C</td>
<td>solvent extraction</td>
<td>GC-FID</td>
</tr>
<tr>
<td>EPH (Extractable Petroleum Hydrocarbons)</td>
<td>Massachusetts</td>
<td>C9-C36</td>
<td>C11-C22</td>
<td>150-265 °C</td>
<td>solvent extraction + SFE fractionation</td>
<td>GC-FID</td>
</tr>
<tr>
<td>ETPH (Extractable Total Petroleum Hydrocarbons)</td>
<td>Connecticut</td>
<td>C9-C36</td>
<td>n/a</td>
<td>n/a</td>
<td>solvent extraction</td>
<td>GC-FID</td>
</tr>
<tr>
<td>GRO (Gasoline Range Organics)</td>
<td>US EPA</td>
<td>C6-C10</td>
<td>n/a</td>
<td>60-170 °C</td>
<td>purge/trap or direct injection</td>
<td>GC-FID</td>
</tr>
<tr>
<td>Wisconsin</td>
<td></td>
<td>C6-C10</td>
<td>n/a</td>
<td>60-170 °C</td>
<td>purge/trap</td>
<td>GC-FID</td>
</tr>
<tr>
<td>PRO (Petroleum Range Organics)</td>
<td>Florida</td>
<td>C8-C40</td>
<td>n/a</td>
<td>n/a</td>
<td>purge/trap</td>
<td>GC-FID</td>
</tr>
<tr>
<td>PVO (Petroleum Volatile Organic Compounds)</td>
<td>Wisconsin</td>
<td>n/a</td>
<td>n/a</td>
<td>60-220 °C</td>
<td>purge/trap</td>
<td>GC-FID</td>
</tr>
<tr>
<td>STARS (Spill Technology and Remediation Series)</td>
<td>New York</td>
<td>n/a</td>
<td>n/a</td>
<td>60-220 °C</td>
<td>purge/trap</td>
<td>GC-FID</td>
</tr>
<tr>
<td>TPH (Total Petroleum Hydrocarbons)</td>
<td>Texas</td>
<td>C5-C35</td>
<td>n/a</td>
<td>n/a</td>
<td>solvent extraction</td>
<td>GC-FID</td>
</tr>
<tr>
<td>Washington</td>
<td></td>
<td>C7-C30</td>
<td>n/a</td>
<td>n/a</td>
<td>solvent extraction</td>
<td>GC-FID</td>
</tr>
<tr>
<td>VPH (Volatile Petroleum Hydrocarbons)</td>
<td>Massachusetts</td>
<td>C5-C12</td>
<td>C9-C10</td>
<td>36-220 °C</td>
<td>purge/trap</td>
<td>GC-FID-FID</td>
</tr>
</tbody>
</table>

*Wisconsin defines the PVOC analyte list as the Wisconsin GRO list minus naphthalene.

*STARS is a State of New York document that provides guidance on the handling, disposal, and/or reuse of excavated petroleum-contaminated soil, with analysis by GC-MS per US EPA Methods 8210 and 8270, modified with short, specific analyte lists.

GRO-Like Analysis by Purge and Trap

Analysis of the volatile portion of fuels/oils typically requires calibration with several n-alkane and aromatic compounds. Some UST programs also require testing for lower molecular weight n-alkanes such as pentane, and for oxygenates such as methyl tert-butyl ether (MTBE). Figure 1 shows a GRO-like chromatogram that includes an analyte list combined from several methods.
The analysis of soil samples often involves a methanol extraction, resulting in a large amount of methanol being transferred to the purge vessel. If retained by the purge trap, methanol can interfere with the detection of early eluting compounds when the trap is desorbed to the GC. The “M” purge trap is specially designed to retain the lighter analytes (pentane and MTBE), but not a significant amount of methanol. A VOCOL™ column was selected due to its ability to provide a short run time while maintaining resolution of critical pairs.

GRO-Like Analysis by Direct Injection

Most GRO-like methods require a purge and trap technique for sample introduction into the GC. US EPA Method 8015 also allows direct injection to be used in some instances (such as for high level samples). Figure 2 shows a chromatogram of our EPA GRO Mix. An SLB™-5ms column with a 1.0 µm film was used to help focus and retain 2-methylpentane.
DRO-like Analysis

Methods for DRO-like are not too different from other work typically performed by environmental laboratories, requiring a solvent extraction and a concentration step prior to GC analysis. The main difference is in the data processing. Figure 3 shows a DRO-like chromatogram with 10 analytes, a surrogate, and an internal standard. A short, narrow bore SLB-5ms column was used to reduce analysis time to less than 15 minutes.
TPH Analysis

Figure 4 shows the analysis of C6-C44 n-alkanes on the SLB-5ms. The composition of the standard represents a carbon range that meets/exceeds the range typically used for TPH analysis. The stability of the SLB-5ms allowed for the use of a high final oven temperature of 360 °C, reducing the elution time of the final C44 hydrocarbon.
Conclusions

The analytical methods required to process samples from a fuel/oil spill incident differ from the methods typical performed in either petroleum or environmental laboratories. Once released into the environment, the fuel/oil is no longer pure enough for pattern recognition, but is too complex for identification and quantitation of individual analytes. A multitude of methods exist to handle these unique sample types.

As confusing as it seems to untangle the many acronyms, there are just three types of analyses: GRO, DRO, and TPH. The published methods are simply variations of these to meet the different analytical needs of the individual agencies. Of utmost importance is to follow the exact methodology required by the regulatory group that will be validating the data reports.

Materials
References

2. Alaska DEC Method AK101, “For the Determination of Gasoline Range Organics” Version 04/08/02
3. Alaska DEC Method AK102, “For Determination of Diesel Range Organics” Version 04/08/02