

Forensic Drinking Water Characterization

Identifying Purgeable and Extractable Chemicals Included in Total Petroleum Hydrocarbon Measurements
Prepared for the Hawaii Department of Health

Introduction

Total Petroleum Hydrocarbon (TPH) analysis is a conventional laboratory technique used for monitoring drinking water samples for petroleum hydrocarbons. TPH analyses conducted using methods like USEPA Method 8015D by Gas Chromatography with a Flame Ionization Detector (GC/FID) provides a bulk measurement of extractable organics detected within a defined carbon range (e.g. gasoline range-GRO, diesel range-DRO, oil range-ORO; Figure 1).

However, GC/FID analysis cannot identify the specific chemicals reported within a bulk measurement. At higher relative concentrations it may be clear that a drinking water sample contains petroleum hydrocarbons, but at low levels confirmation analysis is needed to identify the chemical constituents. When analyzing samples with very low levels of organic matter, it is important to identify the specific chemicals present using a method like GC Mass Spectrometry (GC/MS). GC/MS analysis can be used to determine if low-level organic constituents in a sample are truly petroleum hydrocarbons or are actually related to other non-petroleum organic contaminants or naturally occurring biogenic materials like plant waxes or organic acids.

Figure 1 provides an example of a drinking water sample with both petroleum hydrocarbons and naturally occurring plant waxes. In this example the DRO measurements include impacts from both petroleum and naturally occurring chemicals and contain a high bias due to non-petroleum constituents. Conventional TPH analysis cannot differentiate between these classes of chemicals.

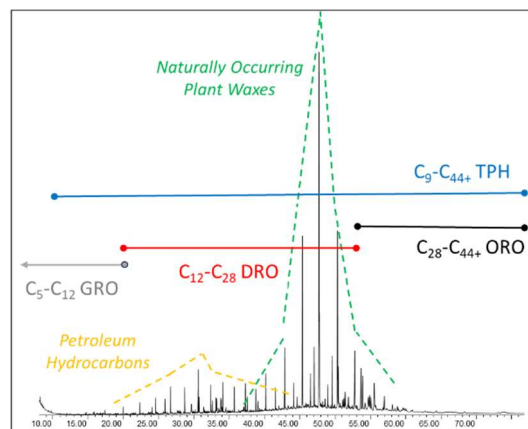


Figure 1. Example Drinking Water GC/FID Chromatogram

Recommended Forensic Analysis for Low Level TPH Characterization

Forensic methods are designed to characterize source materials and are optimized for low level sample analysis. When characterizing low level TPH results it is recommended to follow a tiered analytical approach:

- ❖ Tier I: Modified EPA Method 8015D High Resolution GC/FID Fingerprint
 - High resolution GC/FID fingerprints provide greater separation between carbon ranges and allow for a more accurate assessment of potential source materials.
- ❖ Tier II: Confirmation Testing by GC/MS
 - Samples should then be analyzed by EPA Method 8260D for C₅-C₁₂ purgeable organics and Method 8270E C₈-C₄₄₊ for extractable organics. This type of GC/MS data can be used to perform non-target analysis (NTA) and detect tentatively identified compounds (TICs) that can be used to identify the purgeable, and extractable chemical constituents present in low level TPH measurements. This analysis will help determine if TPH measurements are truly petroleum hydrocarbons or other non-petroleum constituents.
- ❖ Tier III: Petroleum Characterization
 - If petroleum hydrocarbons are present, samples can be analyzed by modified forensic Methods 8260D-PIANO volatile organic compounds and 8270E-Alkylated PAHs. These methods are designed to chemically characterize petroleum hydrocarbon residues, determine source type, and evaluate the degree of environmental weathering.