Novel Method for the Separation and Quantification of Petrogenic and Biogenic Hydrocarbons from a Soil Sample

Soil samples containing high levels of naturally occurring biological organic (biogenic) material can produce false positives when measuring petroleum hydrocarbons (PHCs). If not properly removed from the extract, biogenic materials are included in the reported PHC result, potentially resulting in concentrations above regulatory standards. This may lead to costly remedial activities where no significant PHC impacts are present.

Background

The prescribed methods to remove biogenics may be ineffective where the organic content exceeds the capacity of the clean-up procedures to remove them. In this case, non-petroleum hydrocarbons can be identified by GC/MS analysis but this does not quantify the biogenics’ contribution to the PHC result. The approach often fails due to co-eluting PHCs. Alternative approaches are available, including, among others:

1. Visual evaluation of GC chromatograms for characteristic biogenic hydrocarbon peak patterns;
2. Application of the (Alberta) Biogenic Index Calculation to identify false exceedances; and
3. Comprehensive, 2-dimensional GC evaluation of the proportion of peak area in the 2-D space characteristic of biogenic hydrocarbons.

Although useful for identifying potential biogenic bias, these methods still have limitations:

1. May not optimize isolation of all biogenic materials from petrogenics;
2. Extracts for GC/MS analysis may contain interfering species that preclude accurate identification of biogenic materials; and
3. Results are not obtained in accordance with CCME prescribed procedures.

Bureau Veritas Laboratories Environmental Research & Development group has developed a novel method for the separation and quantification of petrogenic and biogenic hydrocarbons from soil samples. The method is based on an Environment Canada report from 2013 [1], which describes a column fractionation and quantification of petrogenic and biogenic components of bio-diesel. Multiple recovery surrogates are used to verify the efficient separation of the two fractions. The literature method appeared well suited for the range of biogenic materials in a biodiesel is similar to organic content found in soil samples. Additionally, the extraction and quantification protocols described in the Environment Canada method are similar to those prescribed by CCME for analysis of PHCs in soil.

The Fractionation method optimizes the separation of biogenic and petrogenic hydrocarbons from soils with a wide range of organic content and contaminated with different types and amounts of PHCs. A summary of the analytical approach in this method is outlined below.

- The method uses the same hexane solvent extraction approach as prescribed by CCME, but a larger volume of sample is extracted to compensate for high moisture content of organic soils.
- Standard CCME F2-F4 surrogates are added to monitor PHC recovery.
Additional recovery surrogates are added prior to fractionation to monitor its efficiency:
- PHC surrogates: Aliphatic (alkane) + aromatic (PAH)
- Biogenic (BOC) surrogates: Moderate polarity (ester)+ high polarity (sterol)
- The column is eluted with a series of solvents with increasing polarity.
- Fractions containing PHCs are combined and quantified.
- Fractions containing BOCs are combined and quantified.

ADVANTAGES OF THIS METHOD

- Separate quantification of petroleum (PHC) & biogenic (BOC) contents in soils.
- Simplified chromatogram interpretation.
- Use of CCME prescribed methods; Extraction processes and instrumentation are identical to a regular F2-F4 analysis.
- Reporting of biogenic quantified results in petroleum equivalents (calibration is completed following the CCME method for PHC analysis); Use of CCME prescribed methods; extraction processes and instrumentation are identical to a regular F2-F4 analysis.
- Additional recovery surrogate standards for both biogenic and petroleum hydrocarbons demonstrate efficient separation of PHCs from biogenics.
- The biogenic extract is clean, allowing for accurate GC/MS characterization.

LIMITATIONS OF THIS METHOD

It is important to note that this method does not provide complete separation between the biogenic and petrogenic fractions. Indeed, biogenic compounds like monoterpenes, diterpenes and sesquiterpenes are chemically nearly identical to petroleum hydrocarbons and cannot be differentiated using column fractionation. That being said, this novel method significantly reduces biogenic interferences and is an improvement to the existing CCME method in quantifying true petrogenic hydrocarbons.

REFERENCES