TOTAL PETROLEUM HYDROCARBONS

TECHNICAL BULLETIN

Background

Maxxam is often requested by our customers to conduct Total Petroleum Hydrocarbon (TPH) analysis. Due to changes in methodology over time, confusion may exist at the lab and with the customer as to what test or tests the lab should provide.

The initial methodology used for TPH analysis was US Environmental Protection Agency (EPA) Method 418.1, *Petroleum Hydrocarbons (Spectrophotometric, Infrared)*, released in 1978 (equivalent to American Public Health Association (APHA), *Standard Methods for the Examination of Water and Wastewater*, 5520C, first found in the 13th Edition). In this method, the sample is acidified to a low pH (< 2) and serially extracted with Freon. The extract is treated with silica gel adsorbent to remove polar (non-petroleum) hydrocarbons. Infrared analysis of the extract is performed by direct comparison with standards.

In response to the banning of fluorocarbons, the EPA developed gravimetric hydrocarbon methods, Method 1664A for waters and Method 9071B for solids. Notably, they refer to “n-hexane extractable material” instead of TPH. These are essentially equivalent to APHA 5520B and E + F (silica gel treatment).

The issue is further complicated by a current ASTM method, D7678 – 11, *Standard Test Method for Total Petroleum Hydrocarbons (TPH) in Water and Wastewater with Solvent Extraction using Mid-IR Laser Spectroscopy*. In this method, an acidified 900 mL sample of water or wastewater is extracted with cyclohexane. The extract is treated with sodium sulphate and Florisil to remove traces of water, as well as polar substances, thereby producing a solution containing nonpolar material, which is analyzed by mid-infrared laser spectroscopy. As stated in the method, “The nonpolar material is referred to as total petroleum hydrocarbons (TPH).”

The common feature of all these methods is that silica gel treatment is required to remove polar hydrocarbons in order to obtain a TPH (non-polar hydrocarbon) result. TPH is synonymous with Mineral Oil & Grease (MOG).

In 1996 a fundamentally different approach was developed by EPA employing gas chromatography with flame ionization detection (GC-FID) to determine gasoline range organics (GRO) and diesel range organics (DRO). Based on EPA Method 8015A, a purging or headspace method was used to measure C_6-C_{10} volatile hydrocarbons (GRO) and extraction to determine C_{10} – C_{28} hydrocarbons (DRO). Quantitation is achieved by comparison to gasoline and diesel standards. TPH is the sum of the two fractions.

For more information please contact **enviro@maxxam.ca** or **1 800 386 7247**

TOTAL PETROLEUM HYDROCARBONS

Method Comparability

Gravimetric methods determine extracted hydrocarbons (approximately C_{13} and greater). Lighter hydrocarbons are lost in the solvent evaporation process.

Extraction IR methods lose some volatile hydrocarbons during the extraction and silica gel treatment but the loss is much less relative to the gravimetric tests. Thus, depending on the hydrocarbons present, one would expect IR results to be the same or higher than gravimetric. In practice, when only heavier hydrocarbons are present, the opposite may be the case.

The EPA GC-FID method is superior in determining the light hydrocarbons because the sampling and analysis protocols prevent volatilization losses. Extractable hydrocarbons are also accurately determined, although specialized techniques are required to detect the very heavy hydrocarbons in the $C_{60} – C_{100}$ range. The major advantage of the GC technique is that the FID chromatogram provides information on the type of product, whereas the other techniques do not.

Current Status / Recommendations

In Canada, the original GRO / DRO procedure has evolved into a number of regional methods as tabulated below. In every case, the Provincial and Federal Hydrocarbon Guidelines are based on the pertinent GC procedure.

Region	Method	Carbon Ranges	Calibration Standards	Silica Gel Treatment
USEPA	GRO DRO	$C_6 – C_{10}$ $C_{10} – C_{28}$	Gasoline ($C_6 – C_{10}$) Diesel ($C_{10} – C_{28}$)	No
BC	VH EPH	$C_6 – C_{10}$ $C_{10} – C_{19}$ $C_{19} – C_{32}$	Toluene ($C_6 – C_{10}$), 7 n alkanes; $C_{10} – C_{32}$, 3 PAH	Organic soils only
Federal, AB, SK, MB, ON	CCME F1-F4	$C_6 – C_{10}$, $C_{10} – C_{16}$ $C_{16} – C_{34}$, $C_{34} – C_{50}$	Toluene ($C_6 – C_{10}$) nC_{10}, nC_{16}, nC_{34}	Yes
QC	$C_{10} – C_{50}$*	$C_{10} – C_{50}$	#2 Diesel	Yes
QC	TPH**	$C_6 – C_{36}$	MAH #2 Diesel	Yes
Atlantic	Atlantic PIRI	$C_6 – C_{10}$ $C_{10} – C_{16}$ $C_{16} – C_{21}$ $C_{21} – C_{32}$	9 Aromatics 4 n-alkanes, MTBE ($C_6 – C_{10}$) Alkanes $C_{10} – C_{32}$ 6 PAH	Optional
Atlantic	Modified TPH***	$C_6 – C_{32}$	PIRI	Optional

** MDDELCC procedure. Pentane extract, silica gel, GC-FID, used for product identification*

*** Pentane extract, silica gel, GC-FID, used for product identification only*

**** Guidelines for gasoline, diesel / fuel oil, oil. Chromatogram examined to determine hydrocarbon type and Modified TPH compared to that Guideline*

Maxxam currently offers all three method types: gravimetric, IR (using tetrachloroethylene instead of Freon as the extraction solvent) and GC-FID. In addition, calculations of customized hydrocarbon ranges can be provided on request.

Because the GC-FID methods provide accurate $C_6 – C_{10}$ data, product type information and are usable for comparison to remediation guidelines, the pertinent regional method is the recommended procedure for TPH requests. Note that because of different calibration standards, carbon ranges and use of silica gel, the regional GC methods are not directly comparable. Users should be aware that techniques that do not employ silica gel treatment may be biased high if biogenic (polar) hydrocarbons are present.

Either the gravimetric or the IR methods may be required by some customers for historical purposes or for comparison to local guidelines such as sewer use bylaws.

TOTAL PETROLEUM HYDROCARBONS

References

ASTM D7678-11, Standard Test Method for Total Petroleum Hydrocarbons (TPH) in Water and Wastewater with Solvent Extraction using Mid-IR Laser Spectroscopy, ASTM International, West Conshohocken, PA, 2011, **www.astm.org**

Atlantic RBCA, Guidelines for Laboratories, Tier I and Tier II Petroleum Hydrocarbon Methods, Version, 3.0, July 2010, created by the PIRI Analytical Sub-committee.
Available at **http://www.atlanticrbca.com/wp-content/files_mf/1400271724atlanticrbca_guidelines_laboratories_jul10_v3.pdf**

Canadian Council of Ministers of the Environment (CCME). 2001. Reference Method for the Canada-Wide Standards for Petroleum Hydrocarbons (CWS-PHC) in Soil – Tier 1 Method. Endorsed by CCME, April 30-May 1, 2001, Winnipeg.
Available at **http://www.ccme.ca/assets/pdf/phc_standard_1.0_e.pdf**

Centre d'Expertise en Analyse Environnementale du Québec. Identification des produits pétroliers. MA. 408 – IdePet 1.0, Rév. 1, Ministère du Développement durable, de l'Environnement, de la Faune et des Parcs du Québec, 2013.
Available at **http://qsiweb.maxxam.lab:8080/maxxam/$$download.xsp/qsi/5178fe53a6aeb/MA408IdePet10.pdf**

Standard Methods for the Examination of Water and Wastewater. 1971, 13th ed. American Public Health Association, American Water Works Association, & Water Environment Federation

Standard Methods for the Examination of Water and Wastewater. 2012, 22nd ed. Rice, E.W., Baird, R. B., Eaton, A.D., & Clesceri, L.S., eds. American Public Health Association, American Water Works Association, & Water Environment Federation, 5520B Liquid-Liquid, Partition-Gravimetric Method; 5520C Partition-Infrared Method; 5520E Extraction Method for Sludge Samples; 5520F Hydrocarbons.
Available at **http://192.168.18.17/QA/Standard%20Methods%2022nd%20Edition/5520%20Oil%20and%20Grease.pdf**

US Environmental Protection Agency Method 418.1, Petroleum Hydrocarbons (Spectrophotometric, Infrared), Issued 1978.
Available at **http://192.168.18.17/QA/EPA_Methods/EPA/WATER/4XX/418_1.PDF**

US Environmental Protection Agency Method 1664, Revision A: N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry, February 1999.
Available at **http://water.epa.gov/scitech/methods/cwa/oil/1664.cfm**

US Environmental Protection Agency Method 8015A, Nonhalogenated Volatiles Organics by Gas Chromatography, SW-846 Updated I, July 1992. Available at **http://192.168.18.17/QA/EPA_Methods/EPA/SW846/8XXX/8015_A.PDF**

US Environmental Protection Agency Method 9071B, n-Hexane Extractable Material (HEM) for Sludge, Sediment, and Solid Samples, April 1998. Available at **http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/9071b.pdf**

Maxxam
A Bureau Veritas Group Company