

*Replacing the Method 418.1 Test for
Total Petroleum Hydrocarbons Using
Non-Ozone Depleting Substances*

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Agenda

- Total Petroleum Hydrocarbons (TPHs)
- US EPA Test Method 418.1
- Methodologies for Water
- Methodologies for Soil
- Recommendations

Total Petroleum Hydrocarbons (TPHs)

- Describes the 100s of compounds found in oil and petroleum products
 - Carbon Range: C₄ – C₃₅
 - BTEXs
 - Polycyclic Aromatic Hydrocarbons (PAHs)
 - Too many chemicals to analyze individually

TPH Use

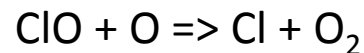
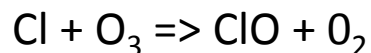
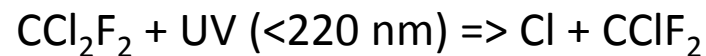
- Used to Quantify Hydrocarbon (HC) contamination in water, soil and sludges
 - Not included as a test for water quality under US Clean Water Act (40 CFR 136)
- **Acceptable Levels** (Oklahoma Dept of Env Quality)
 - Water: 1 mg/L
 - Soil: 50 mg/kg (residential) / 500 mg/kg(industrial)
- Does not describe risk
 - Includes carcinogenic (BTEX) and non-carcinogenic (anthracene, pyrene, and fluoranthene) compounds

US EPA Test Method 418.1

- Only for water and sludges
- Method:
 - Sample acidified to $\text{pH} < 2$
 - Uses CFC-113 to extract HC
 - Measured using Infrared Spectrophotometric against known standards
 - Measures to 1 mg/L
- US EPA removed Method 418.1 on 17 March 2007 (72 Federal Register 11199)
 - Also withdrew Method 413.1 (Oil & Grease)
 - Results no longer accepted by State Agencies

CFC-113 and Montreal Protocol

- Trichlorotrifluoroethane ($\text{Cl}_2\text{FC}-\text{CClF}_2$)
 - Group I Ozone Depleting Substance – 90 year half-life
 - Greenhouse Warming Potential of 4200 ($\text{CO}_2 = 1$)
 - Banned by 2010
- Photochemical breakdown of stratospheric ozone:



Oil in Water and Soils

- Oil compounds exist in 3 phases in Water
 - Free Oil
 - Dissolved (BTEX, PAHs, and Phenols)
 - Dispersed (Droplets)

Fuels

- Gasoline Range Organics (GRO)
 - Carbon Range: $C_4 - C_{10}$
 - Aliphatic alkanes (paraffins) and mono-aromatic HCs (BTEX)
- Diesel Range Organics (DRO)
 - Carbon Range: $C_{10} - C_{40}$
 - Aliphatic, aromatic and heterocyclic HCs

Replacement TPH Methodologies Water

- US EPA Method 1664A
 - Uses n-hexane as solvent extractor
 - Listed as Part 136 Method
- ASTM International Method D7066-04 “Standard Test Method for dimer/trimer of chlorotrifluoroethylene (S-316) Recoverable Oil and Grease and Nonpolar Material by Infrared Determination.”
 - S-316 is a CFC substitute
 - Not listed as a Part 136 Method

US EPA Method 1664A

- Measures Hexane Extractable Material (HEM)
 - Oils, greases, non-volatile compounds
 - Method Detection Limit is 1.4 mg/L
- Sample acidified pH <2
- Sample extracted with n-hexane in a separatory funnel
- Extract is dried over sodium sulfate (NaS)
- HEM is weighed

Intl. Methodologies for Water

- ISO 9377-1
 - Solvent extraction (pentane or hexane)
 - Extraction and Gravimetric
- ISO 9377-2
 - Solvent extraction (pentane or hexane)
 - Gas Chromatography (GC) with flame ionization detector (FID)
- IP 426/98 (UK)
 - Extraction and Infrared Spectrometry

US Methodologies for TPH in Water

- EPA 502.2 & 524.2
 - GC with photoionization detector (GC/PID) and electrolytic conductivity detector (ECD) in series (502.2)
 - GC with mass spectrometry (GC/MS) (524.2)
- State procedures
 - TRNCC Method 1005 (OK & TX)
 - GRO Method (WI)
 - Extractable Petroleum Hydrocarbon (EPH) Method 3 (NJDEP)

Intl. Methodologies for Soil

- ISO 14507
 - Pretreatment of samples for determination of organic contaminants
- ISO 16703
 - GC with FID
 - Not applicable to the quantitative determination of hydrocarbons $< C_{10}$ originating from gasolines
- ISO 9377-2
- ISO 15009
 - GC for VOCs
- ISO 13877
 - Liquid Chromatography for PAHs

US Methodologies for TPH in Soils

- EPA Method 9071B
 - HEM gravimetry
- ASTM D 5765 - 95
 - HEM gravimetry

State Methodologies for TPH in Soils

- TRNCC Method 1005 (TX)
- GRO Method (WI)
- Extractable Petroleum Hydrocarbon (EPH) Method 3 (NJDEP)
- 8002/8000 Methods for GRO & DRO (OK)

Recommendations

- TPH or Petroleum Group Measurement is required to quantify hydrocarbon contamination in water and soil
- Standard Methodology should be established by KEPA for use in Kuwait
 - Not using ODS extractants
- Water
 - US EPA Method 1664A
- Soil
 - US EPA Method 9071B