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: $C_4 - C_{35}$
  - 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 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 (Cl₂FC-CClF₂)
  — Group I Ozone Depleting Substance – 90 year half-life
  — Greenhouse Warming Potential of 4200 (CO₂ = 1)
  — Banned by 2010

• Photochemical breakdown of stratospheric ozone:

  \[ \text{CCl}_2\text{F}_2 + \text{UV} (<220 \text{ nm}) \rightarrow \text{Cl} + \text{CClF}_2 \]

  \[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]

  \[ \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \]
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