SUSPECTED PETROLEUM SPILL – WHAT ANALYS(E)S SHOULD I REQUEST?

1. Do you need to know the TYPE of petroleum product (i.e., gasoline versus motor oil)?
2. Do you need to know the QUANTITY of petroleum product present (i.e., concentration)?
3. Do you need to know if any regulatory LIMITS have been exceeded?

Petroleum Hydrocarbon Mixtures – An Overview

Petroleum products are mixtures of hundreds of organic compounds. The organic compounds fall into two major categories – aliphatic and aromatic. Aromatic compounds are those that contain rings with alternating double bonds (e.g., benzene, benzo(a)pyrene). Aliphatic compounds do not contain any aromatic rings, and may be comprised of single, double or triple bonds and/or non-aromatic rings (e.g., cyclohexane). Most petroleum compounds contain a mixture of aromatic and aliphatic compounds, but the ratio of aliphatic-to-aromatic may not be 1:1. For example, gasoline has a high aromatic content, whereas fuel oils tend to be predominantly aliphatic.

Petroleum products may be roughly defined by their carbon ranges. For example, gasoline has a carbon range of approximately C4 to C12: it is a mixture of hundreds of aliphatic and aromatic compounds each containing between 4 and 12 carbon atoms.

Available Analyses – An Overview

***Ultraviolet (UV) and/or Infrared (IR) Analysis*.** This is a qualitative method that attempts to identify the type of petroleum product present in a sample of water, soil, or waste material. The ability to accurately identify the type of petroleum product present is dependent upon:

1. The amount of product present in the sample. For example, the presence of a "sheen" on a water sample may or may not provide enough material to positively identify the product.
2. The degree of weathering of the product. If the sample has been exposed to water-washing, volatilization, UV or biological degradation, it will be more difficult to positively identify the product.
3. The present of interferences from the sample matrix. For example, surface soil samples can be high in humic acids, which may interfere with the ability to identify the product.

Required bottleware:

Aqueous samples – 2 X 1 L narrow mouth amber glass bottles w/ Teflon-lined screw cap.
Soil samples – 1 x 500 mL amber glass wide mouth jar w/ Teflon-lined screw cap.
Waste samples – 1 x 20 mL scintillation vial with Teflon lined screw cap.

***Oil & Grease (O&G) and/or Total Petroleum Hydrocarbon (TPH) Analysis*.** This is a quantitative method that measures the total concentration of O&G and/or TPH present in the sample. TPH is a subset of O&G, and the analysis is actually performed on the same sample. The sample is first analyzed for O&G, then treated to remove non-TPH materials (e.g., plant and animal oils), then it is re-analyzed for TPH content.

Required bottleware:

Aqueous samples – 2 x 500 mL straight sided clear glass jars with foil or Teflon-lined lids, pH < 2 with 1:1 HCl. The lid size MUST be 70-400.
Soil samples – 1 x 500 mL glass wide mouth jar with foil or Teflon-lined lid.

***Volatile Organic Compound (VOC) Analysis and/or Semivolatile Organic Compound (SVOC) Analysis*.**
These are quantitative methods that measure the concentration of a specific list of compounds ("target" compounds). The target compounds are those for which regulations (Act 2, SDWA, hazardous waste) exist. The regulated compounds are mostly the aromatic components, so the target compound lists do not include many of the aliphatic components typically associated with petroleum hydrocarbon mixtures. VOC/SVOC analysis is done using mass spectrometry, which allows for possible identification of non-target analytes using a spectral database.

1. The choice of VOA versus SVOA depends upon the suspected type of petroleum product.
2. Light-to-mid-weight petroleum products (gasoline, kerosene, diesel fuel, fuel oils 1 through 6) can be detected by VOA analysis. VOA analysis can detect compounds within the approximate range C3 to C14.
3. Mid-to-heavy-weight petroleum products (fuel oils 4 through 6, motor oil, mineral insulating oil, lubricating oil) can be detected by SVOA analysis. SVOA analysis can detect compounds within the approximate range C7 to C35.
4. Very heavy-weight petroleum products (wax, asphalt) may not be amenable to analysis.
5. Non-target compounds (aliphatics) will be reported as Tentatively Identified Compounds (TICs). TICs are not quantitated.
6. VOA/SVOA analysis will NOT identify the type of petroleum product, it will only give information on what compounds are present. For target compounds it will also give the concentration.

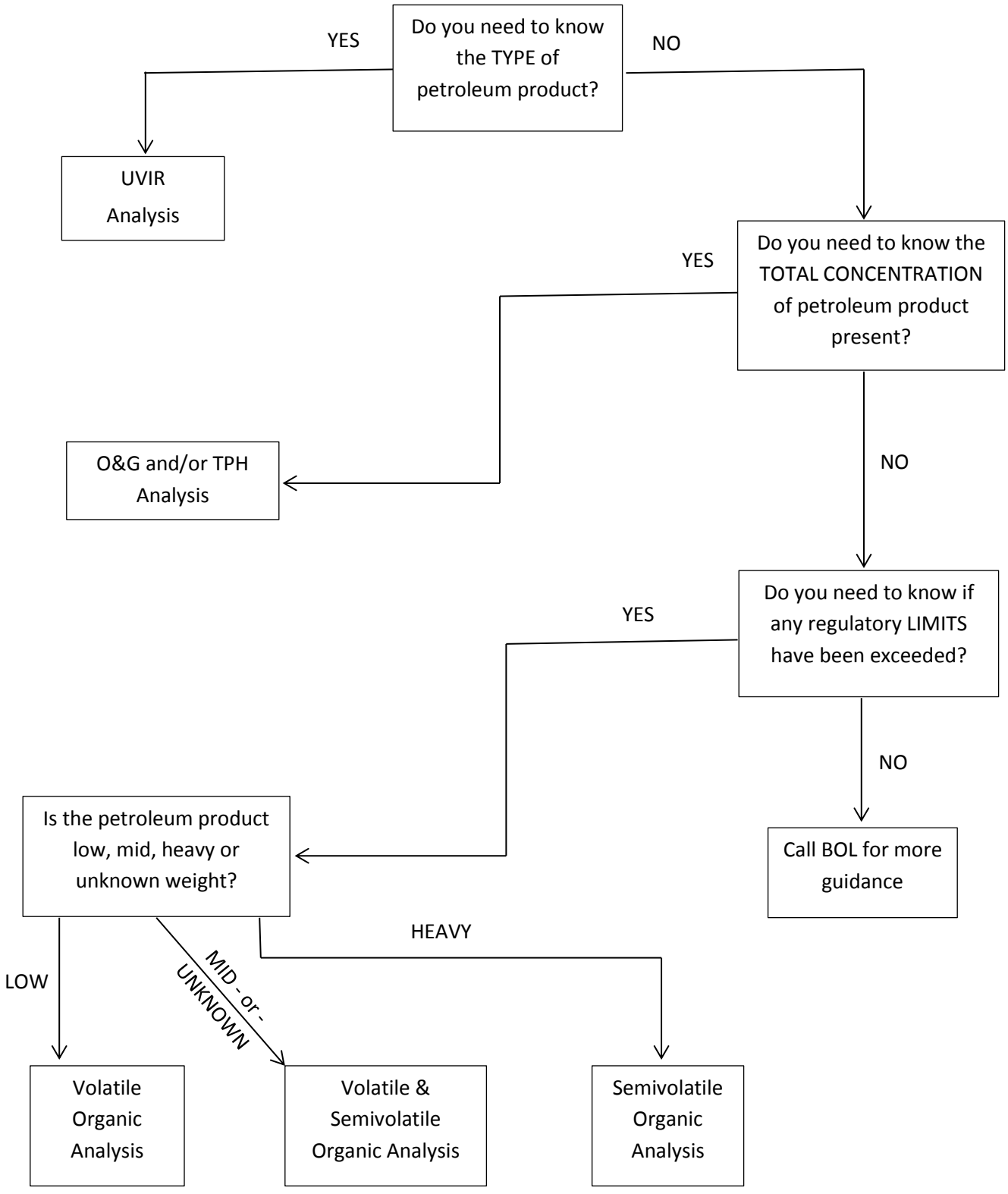
☞ **See Flowchart and Table for a schematic representation of the above information**

Special Case: Source Identification
If you are trying to match spilled material to a suspected source material, the best approach is to use UVIR analysis. Submit a sample of the suspected source material, and also submit samples of the soil or water that has been impacted by the spill. On the Sample Submission Sheet for the impacted soil or water samples write "please match to sample XXXX XXX" and list the collector/sequence number for the suspected source material sample.

Special Case: Aqueous Samples Containing Free Product
For UVIR, O&G, and TPH analysis, collect as much of the free product as possible.
For VOA/SVOA, a large amount of free product (biphasic sample) will complicate the analysis and result in QC failures and elevated reporting limits. Including the free product layer in the analysis of an aqueous sample will yield results that are not truly representative of the aqueous matrix. There are two options:

1. Try to collect only the aqueous fraction, including as little free product as possible.
2. Submit the biphasic sample, but specify how you want the analysis to be performed. Write a note on the Sample Submission Sheet:
   a. "Analyze only aqueous layer"
   b. "Analyze total sample"
   c. "Analyze layers separately" (requires 2 sequence numbers)

PETROLEUM ANALYSIS, FLOWCHART



(See Table on next page for SACs)

PETROLEUM ANALYSIS, VOC/SVOC SAC & BOTTLE INFO

	Drinking Water	Non-Drinking Water	Soil	
Volatile Organic Analysis	TANK2*	TANK1*	TANK3	Short List**
	VOADW*	VOASW*	VOASW	Long List
Semivolatile Organic Analysis	N/A	LOPAH	LOPAH	Short List**
	SV-DW	SV-SW	SV-SW	Long List

*For leaded gasoline spills, also request EDBDW/SW and dissolved/total lead analysis.
**Short list analyses do not report Tentatively Identified Compounds.

Bottleware for VOC/SVOC Analyses

VOADW, VOASW, TANK1, TANK2 (aqueous) – 2 X 40 mL VOA vials, amber glass, Teflon-lined septum screw cap, no headspace. Dechlorinate (if necessary) with 25 mg ascorbic acid. pH < 2 with 1:1 HCl. Ice.

VOASW, TANK3 (soil) – 2 x 5 gram Encore plus 1 X 40 mL VOA vial. No acid. Ice.
Alternatively, submit 2 "high concentration" field preserved vials (available from Ennovative Technologies) plus 1 X 40 mL VOA vial.

EDBDW & EDBSW – 2 X 40 mL VOA vials, amber glass, Teflon-lined septum screw cap, no headspace. Dechlorinate (if necessary) with 4 mg sodium thiosulfate. Ice. No acid.

SV-DW – 2 X 1 L amber glass narrow mouth bottles with Teflon-lined screw cap, cap size 33-430. Dechlorinate (if necessary) with 50 mg sodium sulfite. pH < 2 with 1:1 HCl. Ice.

SV-SW, LOPAH (aqueous) – 2 X 1 L amber glass narrow mouth bottles with Teflon-lined screw cap. Dechlorinate (if necessary) with 80 mg sodium thiosulfate. No acid. Ice.

SV-SW, LOPAH (soil) – 1 X 500 mL amber glass wide mouth bottle with Teflon-lined screw cap. Ice.

Lead (aqueous) – 1 X 125 mL Nalgene bottle. pH < 2 with 1:1 HNO_3. Ice. For dissolved lead, field filter sample before acidification.

Lead (soil) – 1 x 500 mL Nalgene bottle. No acid. Ice.