Priority Pollutant Volatile and Extractable Organics

Priority Pollutant Volatile and Extractable Organics are analyzed using a Gas Chromatograph/Mass Spectrometer (GC/MS). Priority Pollutant Volatile Organics may be analyzed by EPA Methods 624 and 8260, and Priority Pollutant Extractable Organics may be analyzed by EPA Methods 625 and 8270.

For routine monitoring in the petroleum cleanup program, in most instances one or more of these analytical methods may be specified to be performed for only a limited group of chemicals of interest among the chemicals listed in Table A of Chapter 62-770, Florida Administrative Code (F.A.C.) as Petroleum Products' Contaminants of Concern since the analyses should be based on applicable rules and procedures. For example, for BTEX + MTBE or PAHs the analysis request would indicate BTEX + MTBE (EPA Method 8260) and/or PAHs (EPA Method 8270).

These analytical methods may be used for a greater number of chemicals than are recognized as Petroleum Products' Contaminants of Concern; however, a greater scope of analysis using one of these methods should only be specified when there is a recognized regulatory or programmatic reason to determine concentrations of a broader range of chemicals of concern. Three examples of circumstances in which a greater range of analysis would be necessary are:

1) For aqueous and solid samples during assessment of used oil discharges, where EPA Methods 8260 and 8270 should be used for both media.
2) For aqueous samples, to comply with the National Pollutant Discharge Elimination System (NPDES), where federal regulations specify that analytical methods for organic chemical analyses of municipal and industrial wastewater, such as EPA Methods 624 and 625, must be used.
3) For solid samples, to comply with current preapproval requirements for analyses of backfill samples, where EPA Methods 8260 and 8270 are used.

Each method includes a basic list of analytes. In each pair of equivalent methods, 624 has a shorter list than 8260 and 625 has a shorter list than 8270, but it is possible for laboratories to be certified for additional analytes under any of these analytical methods or to be certified for some of these analytes only under a different analytical method (a good example are the analytes found in the certification page under "Pesticides-Herbicides-PCBs") or under a laboratory-specific SOP. Two examples are provided below to scope these analyses depending on the laboratory's certifications. The four attached pdf's provide the basic list of analytes in each of the methods. Normally (especially for EPA Method 8270), laboratories are certified for a smaller number of analytes for solid samples than for aqueous samples.

The two main groups of chemicals listed in EPA Methods 624 and 8260 are volatile organic aromatics (VOAs; chemicals with one benzene ring in the molecule), and volatile organic halocarbons (VOHs; chemicals with Chlorine and/or Bromine and/or Fluorine in the molecule). Important VOHs outside of petroleum cleanup are common chlorinated solvents such as Trichloroethene (TCE) and Tetrachloroethene (PCE or PERC), and their by-products such as Vinyl chloride. Some VOHs are used as solvents in laboratories to perform extractions, and it is not uncommon to see them (especially Methylene chloride) detected in laboratory blanks.

The main groups of chemicals listed in EPA Methods 625 and 8270 are Polycyclic Aromatic Hydrocarbons (PAHs), Organochlorine Pesticides, Polychlorinated Biphenyls (PCBs, also known as Aroclors), and Phenols. The list of EPA Method 8270 also includes Organophosphorus Pesticides, etc.

Unless specified otherwise, Groundwater and Soil Cleanup Target Levels (CTLs) are referenced in Chapter 62-777, F.A.C. for all the individual analytes listed below.

EPA Method 624: This method lists 31 chemicals on page 1, including six VOAs, many VOHs, and one ether.

a) VOAs: Benzene, Ethylbenzene and Toluene are listed. Total Xylenes is not listed, but most laboratories are certified for it under this method.

b) VOHs: 1,2-Dichloroethane (EDC) is listed. It was used as an additive in leaded gasoline.

c) Ethers: MTBE is not listed and only a few laboratories are certified for it under this method.

EPA Method 8260C: This method (not counting surrogates and internal standards) lists 105 chemicals on pages 1-4, including several VOAs, many VOHs, several alcohols, Naphthalene, five ethers, and a few amines and aldehydes. Paragraph 1.3 (on pages 4-5) lists several additional chemicals "amenable to analysis by Method 8260." Note: Eight analytes (including Naphthalene) are listed also in EPA Method 625 and 12 analytes (including Naphthalene) are listed also in EPA Method 8270D.

a) VOAs: Benzene, Ethylbenzene, Isopropyl benzene (=Cumene), Toluene, and o-, m- and p-Xylene are listed [laboratories should be certified for, and report, Total Xylenes]. Paragraph 1.3 lists 1,2,4- and 1,3,5-Trimethylbenzene, both of which are common constituents of petroleum products.

b) VOHs: 1,2-Dibromoethane (EDB) and 1,2-Dichloroethane (EDC) are listed. Both were used as additives of leaded gasoline for on-road motor vehicles (EDB and EDC had other uses and EDB is currently used in aviation gasoline). Only one laboratory has shown the capacity of reaching a Practical Quantitation Limit (PQL) of 0.02 µg/L for EDB by EPA Method 8260 and therefore most laboratories should analyze EDB by EPA Method 504.1 or 8011.

c) Ethers: MTBE and the ethers that replaced MTBE in unleaded gasoline, such as Diisopropyl ether (DIPE), Ethyl tertiary butyl ether (ETBE), and Tertiary amyl methyl ether (TAME) are listed. Groundwater CTLs and Soil CTLs have not been published for the latter three ethers at this time.

d) Alcohols: tert-Butyl Alcohol (TBA), Ethanol and Methanol are listed.

EPA Method 625: This method lists 61 Base/Neutral Extractables on Table 1 (pages 18-19) and 11 Acid Extractables on Table 2 (page 20), including most PAHs, many Organochlorine Pesticides, PCBs, Phenols, Phthalate Esters, Haloethers, etc. Nine additional extractables are listed on Table 3 (page 20), but the table lists the preferred methods to analyze those chemicals. For Petroleum Cleanup purposes, when EPA Method 625 is scoped to comply with NPDES requirements, analyses for chemicals not listed on Tables 1 and 2 are not necessary. Note: Eight analytes (including Naphthalene) are listed also in EPA Method 8260C.

a) PAHs: 1- and 2-methylnaphthalene are not listed in the method, and very few laboratories are certified for the chemicals under EPA Method 625.

EPA Method 8270D: This method (not counting surrogates) lists 238 chemicals on pages 1-7, including most PAHs, many Organochlorine Pesticides, PCBs, Phenols, Phthalate Esters, and

Haloethers, but also Organophosphorus Pesticides, Carbamates, etc. Note: Twelve analytes (including Naphthalene) are listed also in EPA Method 8260C.

a) PAHs: 1-methylnaphthalene is not listed in the method, and very few laboratories are certified for the chemical under EPA Method 8270.

If it is necessary to scope the full list of any of these methods in a work order or task assignment, remember that some laboratories are certified for more analytes than others and no laboratory certified in Florida is certified for the entire list of EPA Method 8270 chemicals. Therefore, from a practical perspective there should not be an expectation that every chemical on the EPA Method 8270 list will be represented in the analytical results. However, the intent of the analysis needs to be considered and the laboratory capabilities should be examined before selecting a laboratory which will provide meaningful results. Using the NELAP certification provided by the contractor, check whether the laboratory is certified for the major groups of analytes and for all the analytes critical in petroleum cleanup or to meet NPDES requirements or backfill sampling considerations. For example, many laboratories are only certified for PCBs under EPA Method 608 and/or EPA Method 8082, and for Organochlorine Pesticides under EPA Method 608 and/or EPA Method 8081. Therefore, to comply with the one-time EPA Method 625 requirement for NPDES, usually it will be necessary to scope EPA Method 625 and EPA Method 608. Since the current fixed price for Priority Pollutant Extractable Organics in aqueous samples ($303.31) is for the full list, Petroleum Cleanup should not pay extra for EPA Method 608. Likewise, for used oil contamination and for backfill often it is necessary to scope EPA Method 8270 and EPA Methods 8081 and 8082. Since the current fixed price for Priority Pollutant Extractable Organics in solid samples ($298.24) is for the full list, Petroleum Cleanup should not pay extra for EPA Methods 8081 and 8082.

When BTEX/MTBE and VOH analyses are scoped, it is common for laboratories to run a full EPA Method 8260 and report all the priority pollutant volatile organics. When that happens, it is not uncommon for contaminants such as 1,2,4- and/or 1,3,5-Trimethylbenzene and/or Cumene (not listed on Table A of Chapter 62-770, F.A.C.) to be detected. Since these chemicals are constituents of petroleum products and most likely they are derived from the petroleum product discharge, they must be addressed in the cleanup of that discharge if the concentrations reported were above their Groundwater CTLs.