Overview of VPH Methods

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Current VPH Method (1998; updated 2004)

GC with in-series photoionization and flame ionization detectors (PID/FID)

New VPH by GC/MS Method (2017)

GC with MS detector (based on EPA Method 8260 for VOCs)

A different way to "skin the cat"

Objective of a "VPH" test:

Generate data to support MassDEP petroleum hydrocarbon risk assessment process

For volatile petroleum hydrocarbons (in soil or water):

- Quantify aliphatic hydrocarbons with between
  - 5 and 8 carbon atoms; and
  - 9 and 12 carbon atoms
- Quantify aromatic hydrocarbons with between 9 and 10 carbon atoms.

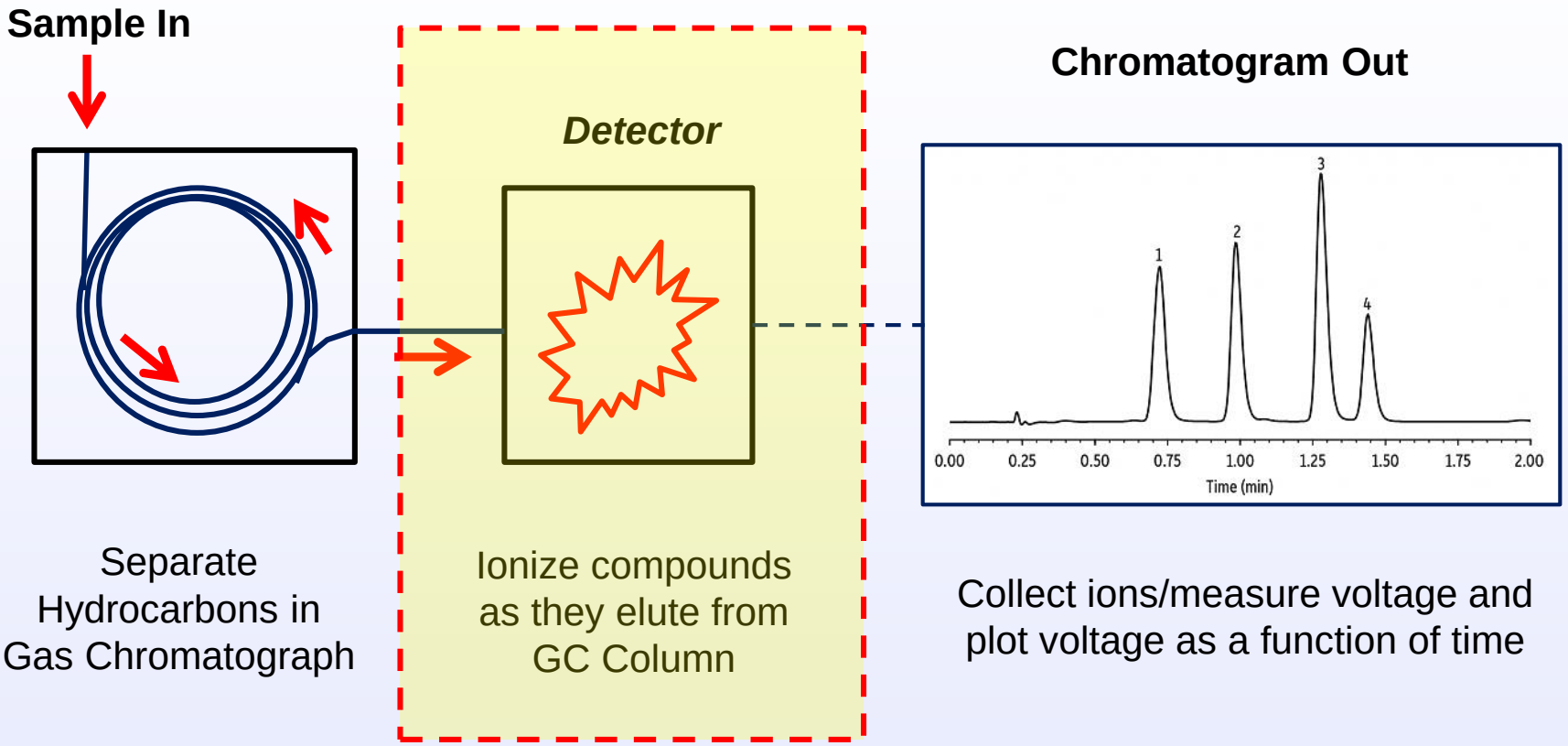
Perfect Method:

- Accurate
- Simple
- Cheap

Striking a Balance….

- Accurate enough
  - ➢ err on the side of being health-protective, without being overly conservative
- Moderately complex
  - ➢ unconventional procedures
  - ➢ data adjustment steps
- Reasonably priced

Both Methods Use Same Conceptual Approach



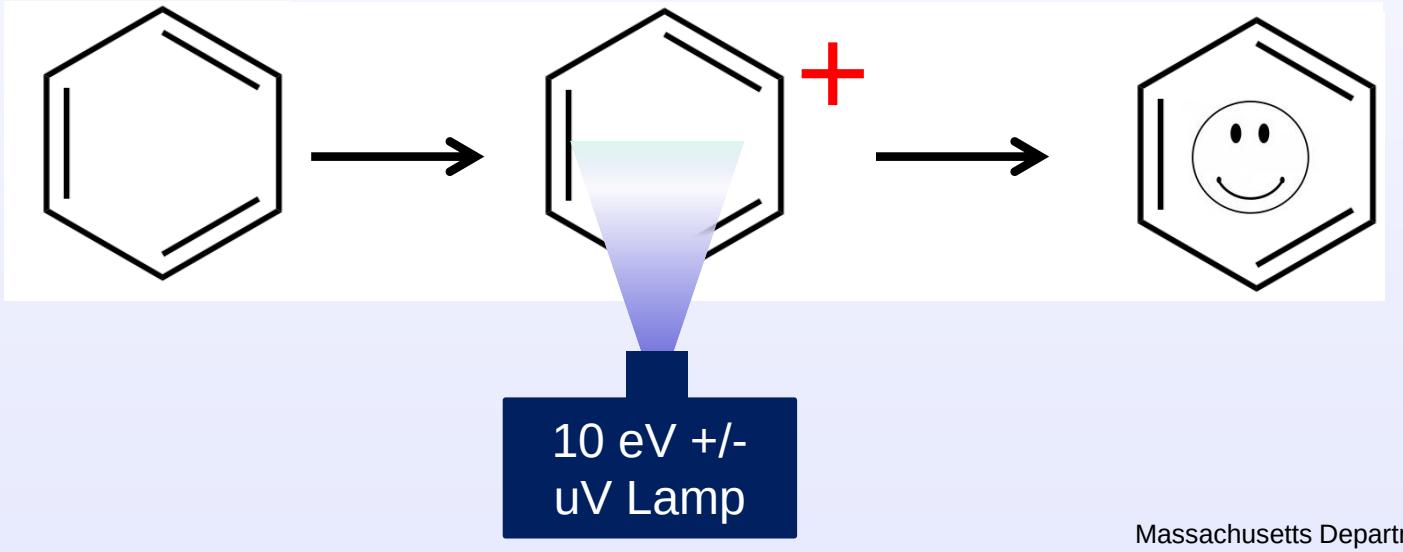
Detector Selectivity helps us tease out what we need to know about sample chemistry……

…….along with a bunch of simplifying assumptions and decisions

Detectors

Photoionization Detector (PID)

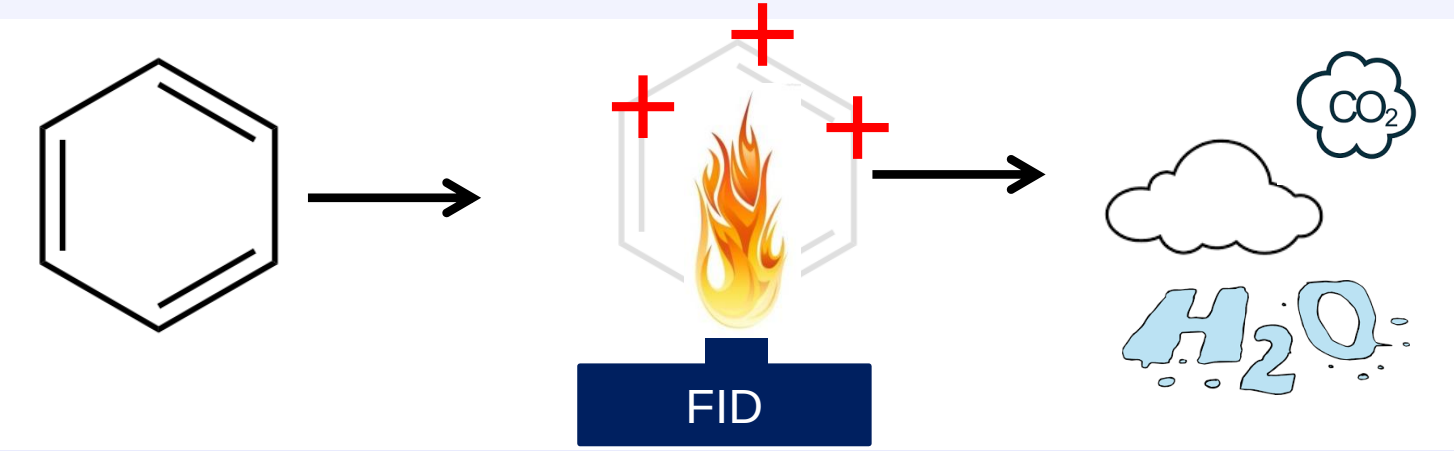
- ionizes compounds by “knocking” off an electron
- at a given PID energy (eV), not all compounds are ionized (“selective” detector – compounds with double bonds more easily ionized)
- non destructive – compounds in sample are not destroyed



Detectors

Flame Ionization Detector (FID)

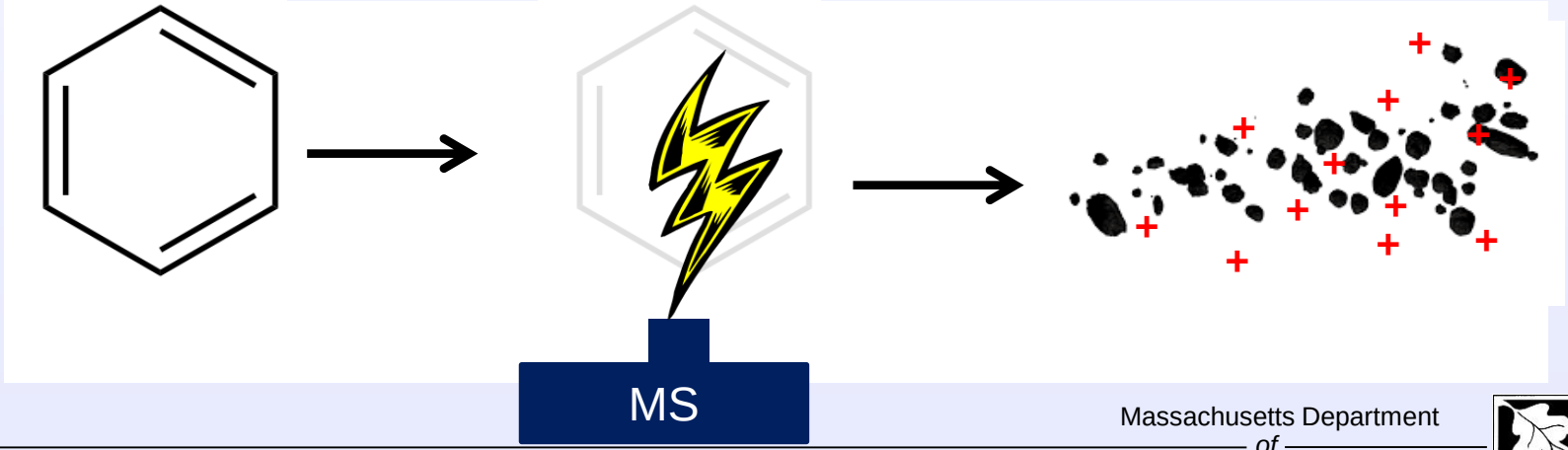
- compounds are combusted (and destroyed) in a hydrogen flame
- ions are produced in the combustion process
- the amount of ions produced is proportional to mass of compound
- most organic compounds produce the same number of ions (“universal” detector”)



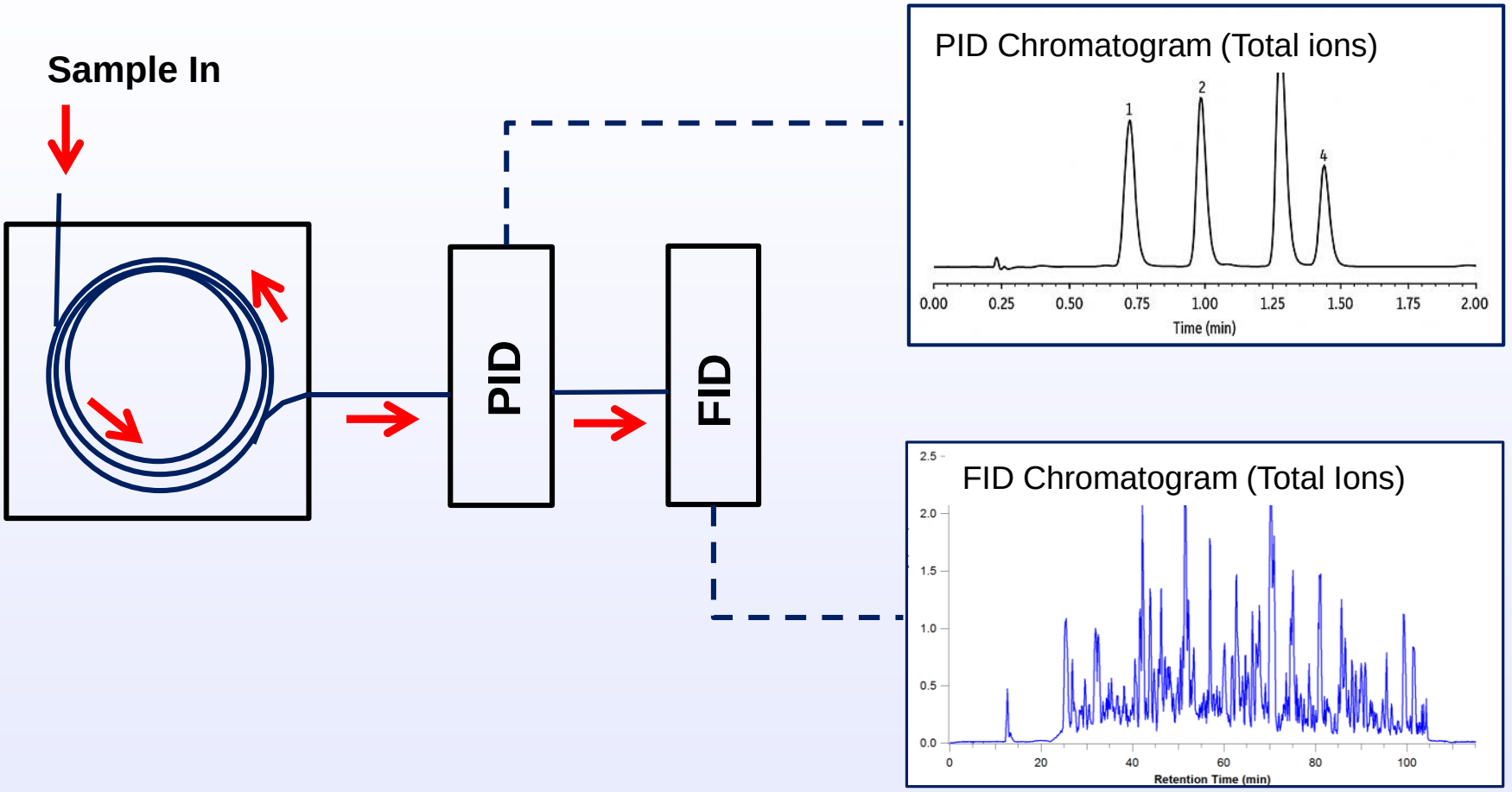
Detectors

Mass Spectrometer (MS)

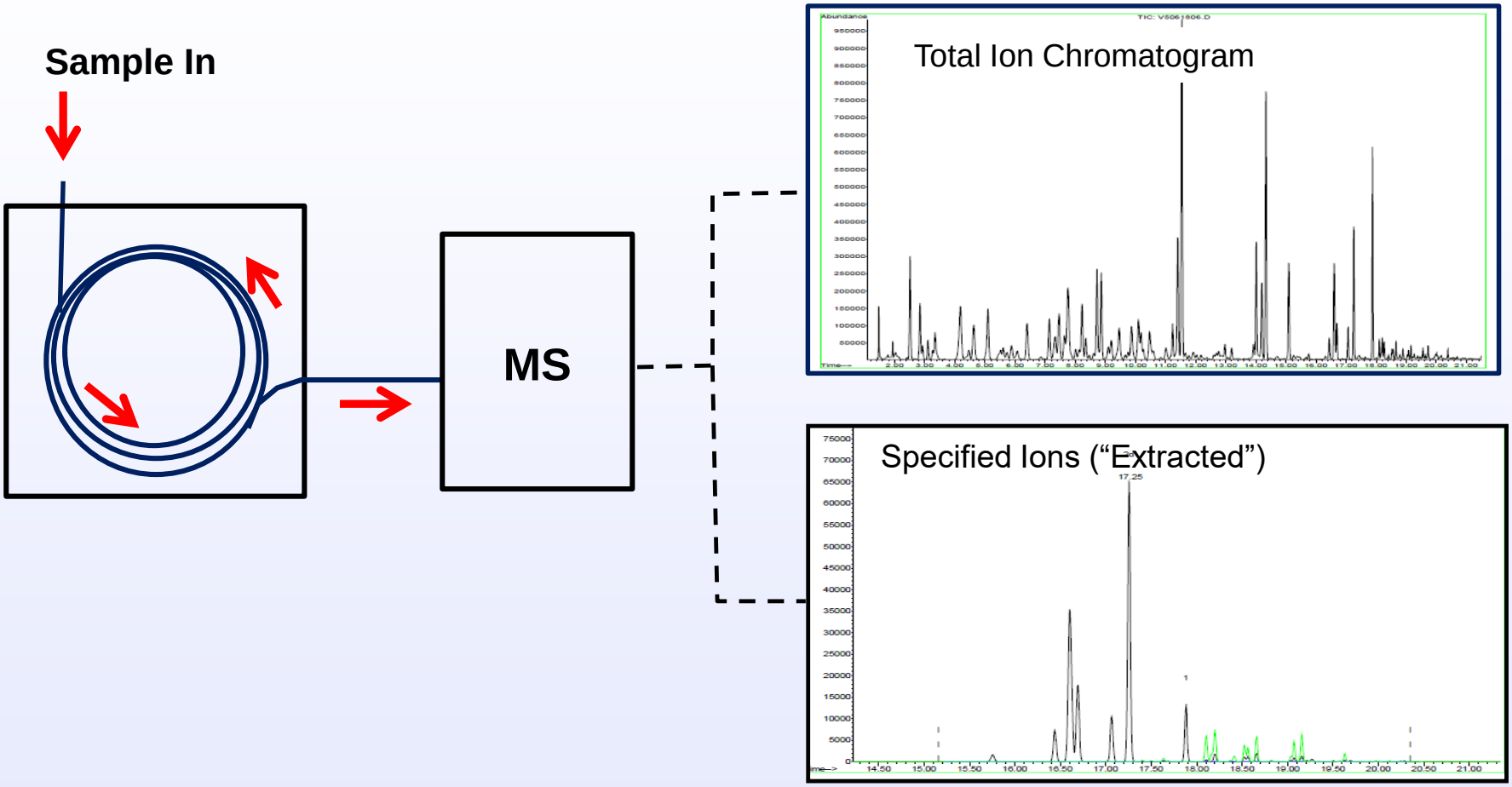
- ionizes compounds by bombarding them with electrons, “blowing them apart” into smaller particles with a certain mass and charge (usually +1)
- Ions are passed through a “mass filter” that allows them to “hit” a detector element one at a time, based upon their mass and charge (“m/z”)
- The ratio of the ions (m/z) is a unique “fingerprint” of the compound
- The amount of ions is proportional to the amount of compound present



VPH by GC/PID/FID



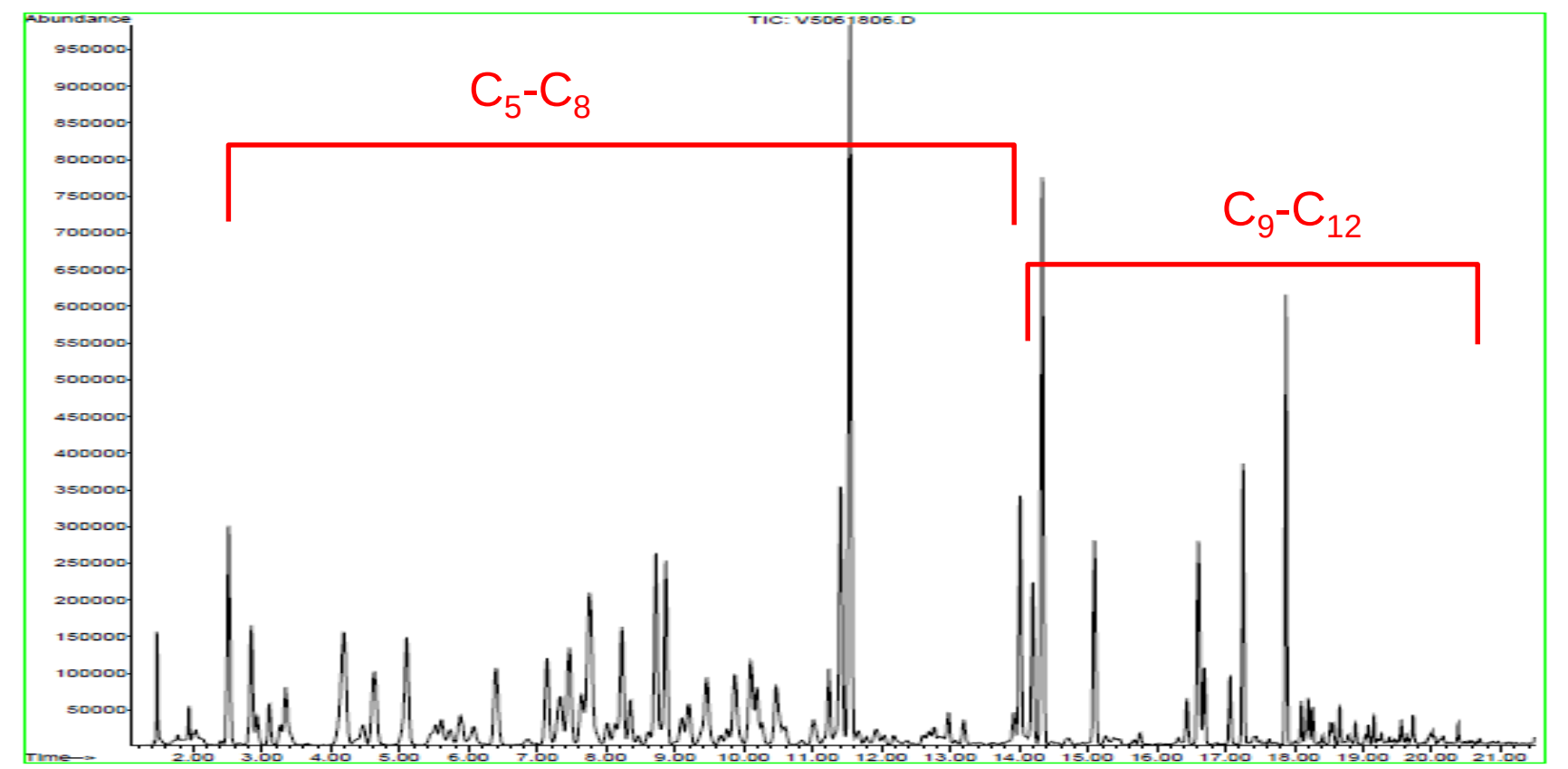
VPH by GC/MS


Sample In
MS
Total Ion Chromatogram
Specified Ions (“Extracted”)

VPH – just 4 steps!

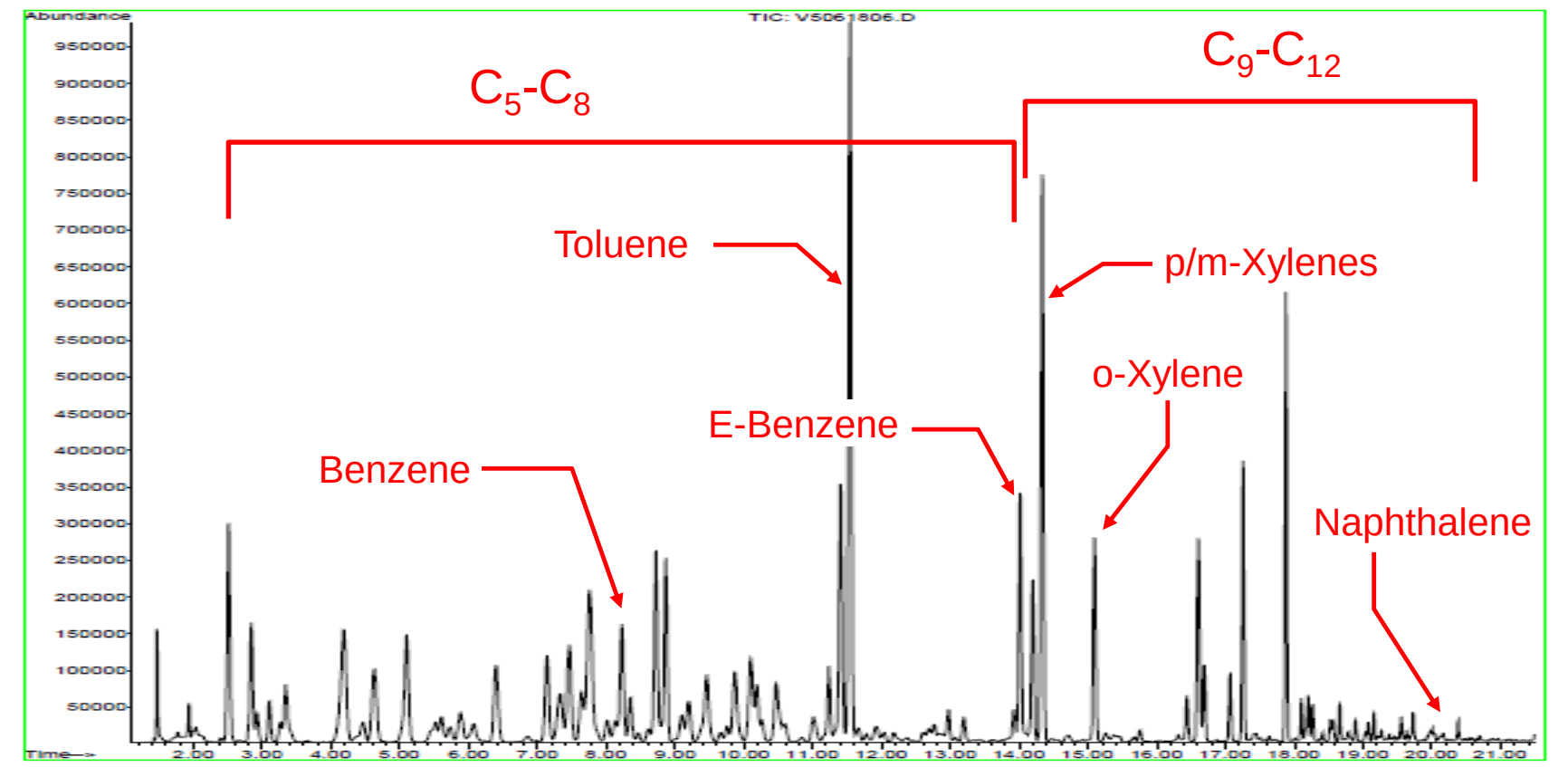
Step 1

Quantify all petroleum hydrocarbons (aliphatic and aromatic) that have between 5 and 8 and between 9 and 12 carbon atoms (*more or less*). **FID or MS Detector**



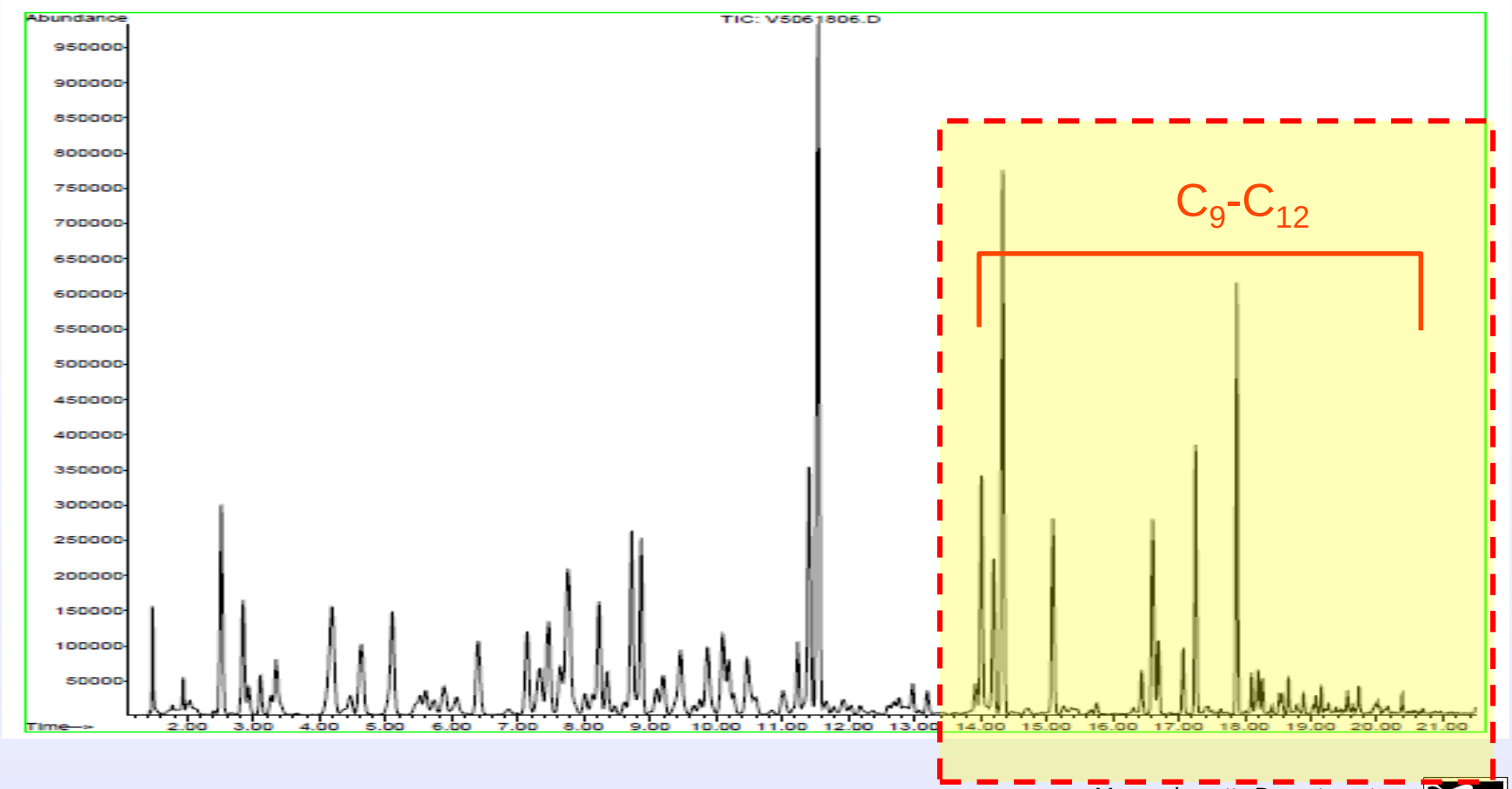
Step 2

Quantify specified Target Analytes (*MtBE, BTEX, and Naphthalene*) **PID or MS Detector**



Step 3

Quantify aromatics with between 9 and 10 carbon atoms
(*C_9-C_{10} Aromatic Hydrocarbons*) **PID or MS Detector**

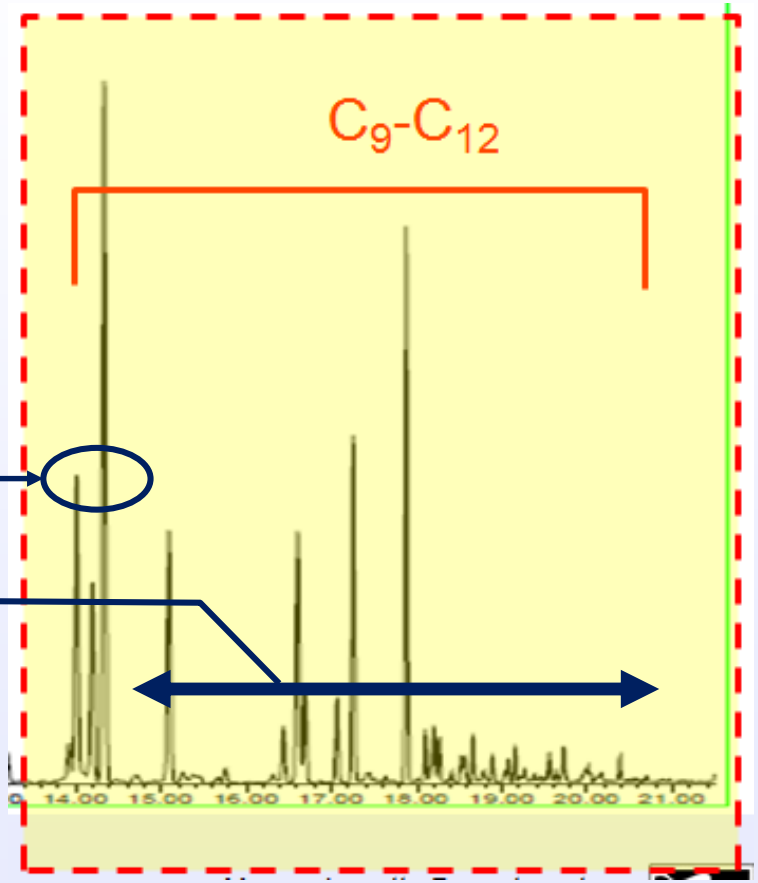


Step 3

Quantify aromatics with between 9 and 10 carbon atoms (*C_9-C_{10} Aromatic Hydrocarbons*)

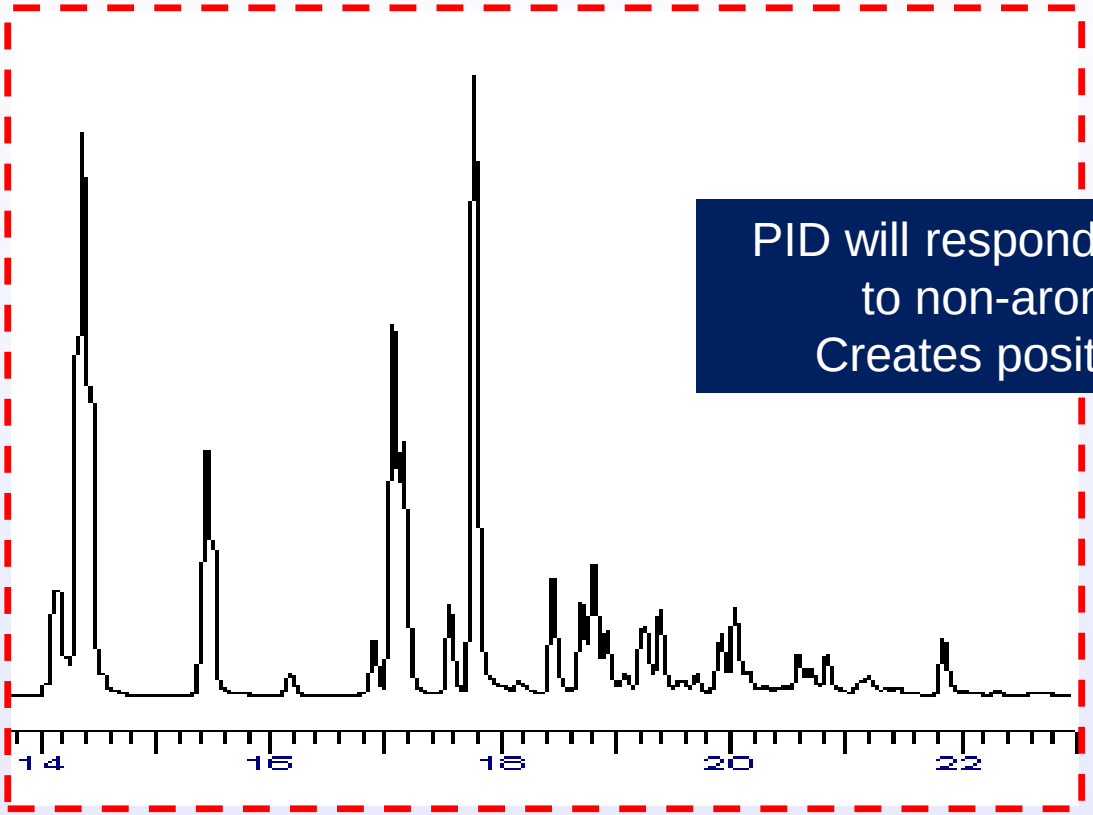
Xylenes (C_8 Aromatic)

C_9 – C_{10} Aromatics



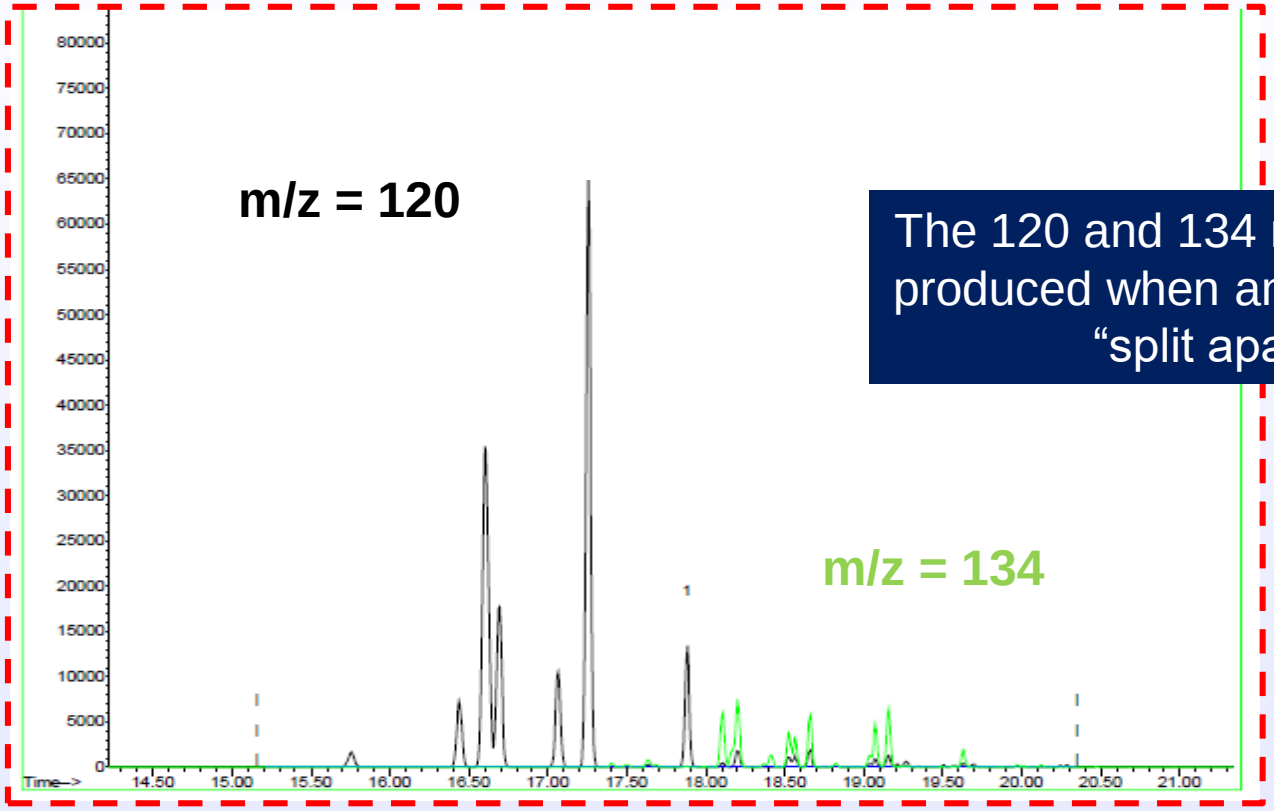
- 1,2,4-Trimethylbenzene
- 1,3,5-Trimethylbenzene
- 1-Methyl-3-Ethylbenzene
- 1-Methyl-4-Ethylbenzene
- 1-Methyl-2-Ethylbenzene
- Propylbenzene
- 1,2,3-Trimethylbenzene
- 1,2-Diethylbenzene
- 1,2-Dimethyl 4-Ethylbenzene
- Isopropylbenzene (Cumene)

Step 3 - Using PID response in GC/PID/FID Method



PID will respond somewhat
to non-aromatics
Creates positive Bias

Step 3 - Using “extracted ions” in GC/MS Method)



The 120 and 134 m/z ions are produced when an aromatic is “split apart”

Step 4 - Data Adjustments

C_5-C_8 Aliphatics = (Total C_5-C_8 Hydrocarbons) – (MtBE/B/T)

C_9-C_{12} Aliphatics = (Total C_9-C_{12} Hydrocarbons) – (E/Xylenes) – (C_9-C_{10} Aromatics)

C_9-C_{10} Aromatics = C_9-C_{10} Aromatics

MtBE/BTEX/N = MtBE/BTEX/N

Either method may be used to fulfill the risk assessment/data submittal requirements of the MCP

OK….. Which one should I use?

Both methods have (systemic/added) biases, to meet the objective of being moderately but not overly conservative (i.e., health protective)

These biases were explored in detail in a "Round Robin" testing program, in which 5 volunteer labs analyzed a water and soil sample by both the GC/PID/FID and the draft GC/MS procedure

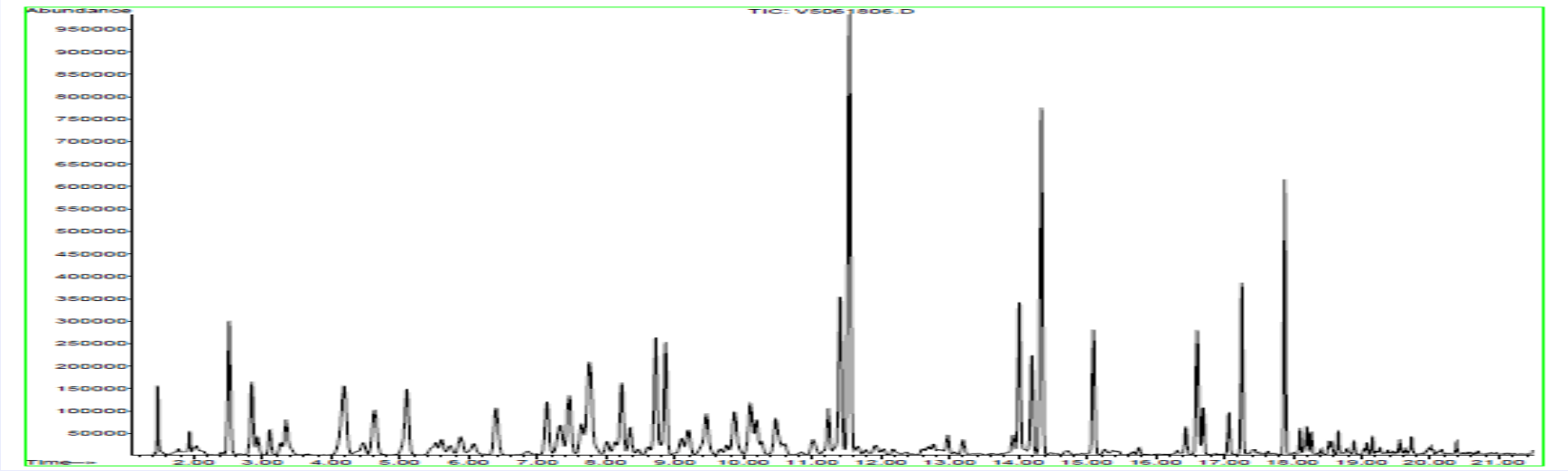
The bottom line: overall, the data are "comparable", in that either will likely lead to the same outcome (i.e., on whether remediation/AUL is required).

But there are some differences….

VPH by GC/PID/FID biases:

- PID will respond to aliphatics to some degree, which will *over-quantify* concentrations of C_9-C_{10} Aromatic Hydrocarbons (perhaps by 30% +/- in soils)

  moderately conservative and thus health protective; should not be an issue in water samples



VPH by GC/PID/FID biases:

- Subtracting inflated C_9-C_{10} (PID) Aromatic value from C_9-C_{12} FID value will lead to *under-quantified* values for C_9-C_{12} Aliphatics

  non-conservative but generally not significant as C_9-C_{12} Aliphatics are rarely risk drivers at sites

	GW-1	S-1/GW-1
C_5-C_8 Aliphatics	300 µg/L	100 mg/kg
C_9-C_{12} Aliphatics	700 µg/L	1000 mg/kg
C_9-C_{10} Aromatics	200 µg/L	100 mg/kg

VPH by GC/PID/FID biases:

- PID can also *over-quantify* concentrations of Target Analytes (e.g., BTEX) if there are co-eluting peaks

  health protective; not a big issue in water samples

  On the other hand, since concentrations of (PID) Target Analytes are subtracted from the (FID) aliphatic range concentrations, this could lead to an under-quantification of C_5-C_8 and/or C_9-C_{12} Aliphatics

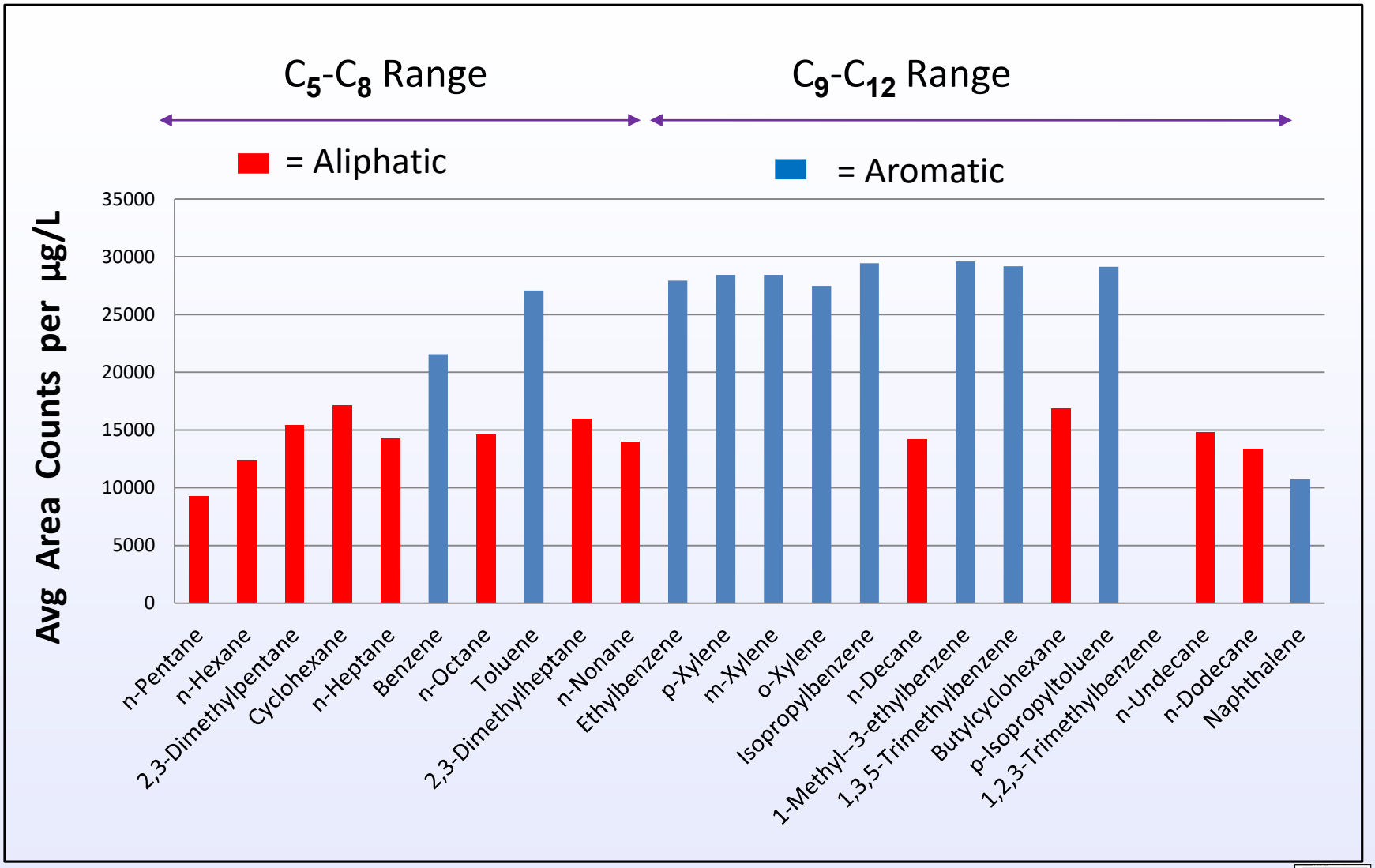
  Generally not a big deal

VPH by GC/MS biases:

- Tends to over-quantify C_9-C_{12} Aliphatic Hydrocarbons, because MS is not a “universal” detector like the FID, and commonly used GC/MS models seem to respond to aromatic compounds better than aliphatic compounds.

  health protective; not a big issue in water samples; generally not significant in soil samples as C_9-C_{12} Aliphatic are rarely risk drivers at sites

Average Total MS Ion Response for VPH Calibration Standard



Summary of Comparative Biases and Capabilities

	VPH by GC/PID/FID	VPH by GC/MS
Target Analytes	Possible High Bias	No Bias
C_5-C_8 Aliphatics	Possible Low Bias	No Significant Bias
C_9-C_{12} Aliphatics	Low Bias	Likely High Bias
C_9-C_{10} Aromatics	High Bias (perhaps 30%)	No Significant Bias
ID Non Petro Compounds?	No	Yes

For much more detail on the performance and biases of each method see:

"Evaluation of MassDEP Volatile Petroleum Hydrocarbon (VPH) Methods: VPH by GC/PID/FID and VPH by GC/MS, June 2016", on the MassDEP web site under "VPH/EPH"