

## Optimizing Massachusetts Volatile Petroleum Hydrocarbon GC Analysis

Total Petroleum Hydrocarbon (TPH) analysis allows the characterization of dozens of commercially available petroleum products, which are the most prevalent environmental pollutants. The two fractions of TPH—volatile gasoline range organic (GRO) compounds, also called petroleum volatile organic compounds (PVOC), and the semivolatile diesel range organic (DRO) compounds—are analyzed differently depending on their boiling point ranges.

Typical methods for the identification of gasoline use early and late eluting compounds to determine an analytical window for total gasoline quantitation. Then, GC analysis uses pattern recognition, the specific ratio of peaks that make up a particular compound, to identify a fuel. If a pattern falls within this window, it may be reported as gasoline and quantified. Difficult matrices can result in misidentification or poor quantitation of the sample, and environmental degradation (i.e., weathering) further complicates this analysis.

On January 1, 1998, the Massachusetts Department of Environmental Protection (MADEP) promulgated a new method, known as Volatile Petroleum Hydrocarbons (VPH) to better quantify gasolines. This method identifies and evaluates PVOCs by differentiating and characterizing the aromatic and aliphatic fractions of gasoline using a photo-ionization detector (PID) and a flame ionization detector (FID) in series. The data generated from this method will aid in evaluating human health hazards that may result from exposure to PVOCs. Other states in the US and provinces in Canada have adopted the VPH method for use in remediation, site characterization, and toxicity data (mixtures for other methods are listed in the UST Product Listing, lit. cat. #59617-A).

### Difficulties with the Analysis

A large proportion of VPH samples are soil. The soil is weighed in the field and an equal amount of methanol is added at the time of sampling. 100uL of methanol extract is added to 4.9mL of water and then is purged. One problem with this analysis is that most purge-and-trap concentrators were not designed to have large amounts of methanol purged onto their absorbent beds. The VOCARB™ 3000 and VOCARB™ 4000 traps have difficulty retaining *n*-pentane and 2-methylpentane after repeated exposure to methanol, causing poor linearity of these compounds. We suggest using a BTEX trap because of its non-polar properties. You will experience a slight decrease in response for methyl-*tert*-butyl-ether, but it will not compromise your detection limit.

### Column Selection

All purge-and-trap methods for this analysis result in broad, early eluting peaks. Therefore, choosing the right chromatographic column can prevent coelutions and poor quantitation. Many columns may drastically change the quantitation of aliphatic and aromatic compounds, or suffer from poor resolution of methanol and methyl-*tert*-butyl-ether or from poor separation of pentane and 2-methylpentane. For optimized separation of light hydrocarbons and light gas additives, use the Rtx®-502.2 column specified in the VPH method.

Figure 1 shows the separation of VPH compounds on an Rtx®-502.2 column, using a PID (Figure 1A) and an FID (Figure 1B). The first peak in the chromatogram is methanol. Notice that it is clearly separated from the methyl-*tert*-butyl-ether and *n*-pentane.

Figure 1

To achieve optimum VPH analysis using an Rtx®-502.2 column, use PID for aromatic compounds and FID for aliphatic compounds.

Figure 1A: PID

- |  |                             |
|--|-----------------------------|
| 1. methanol                                | 9. naphthalene (40ng)       |
| 2. methyl- <i>tert</i> -butyl-ether (60ng) | 10. 2,5-dibromotoluene (ss) |
| 3. benzene (20ng)                          |                             |
| 4. toluene                                 |                             |
| 5. ethylbenzene (20ng)                     |                             |
| 6. <i>p</i> + <i>m</i> -xylene (40ng ea.)  |                             |
| 7. <i>o</i> -xylene (40ng)                 |                             |
| 8. 1,2,4-trimethylbenzene (40ng)           |                             |

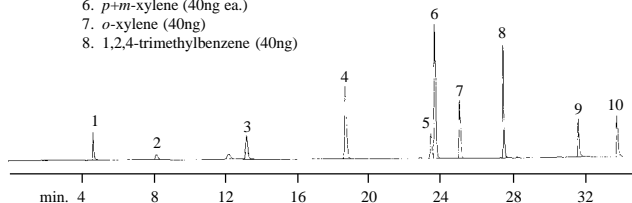
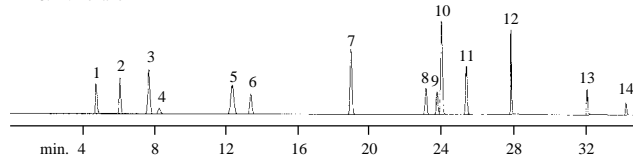


Figure 1B: FID

- |  |  |
|--|--|
| 1. methanol                                | 9. ethylbenzene (20ng)                     |
| 2. <i>n</i> -pentane (40ng)                | 10. <i>p</i> + <i>m</i> -xylene (40ng ea.) |
| 3. 2-methylpentane (60ng)                  | 11. <i>o</i> -xylene (40ng)                |
| 4. methyl- <i>tert</i> -butyl-ether (60ng) | 12. 1,2,4-trimethylbenzene (40ng)          |
| 5. 2,2,4-trimethylpentane (60ng)           | 13. naphthalene (40ng)                     |
| 6. benzene (20ng)                          | 14. 2,5-dibromotoluene (ss)                |
| 7. toluene                                 |  |
| 8. <i>n</i> -nonane                        |  |



105m, 0.53mm ID, 3.0µm (cat.# 10910). **Concentration:** on-column at levels listed; **Oven temp:** 45°C to 90°C @ 3°C/min., to 140° @ 5°C/min., to 230°C @ 45°C/min. (hold 8 min.); **Carrier gas:** helium @ 15mL/min.; Tekmar® Model LSC 2000; **Trap:** BTEX; **Purge:** helium @ 40mL/min. for 11 min.; **Dry purge:** 2 min.; **Desorb preheat:** 245°C; **Desorb:** 2 min. @ 250°C; **Bake:** 6 min. @ 260°C.

Chromatograms courtesy of Severn Trent Laboratories, Burlington, VT.

The PID is used to identify target VPH analytes, defined as benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, naphthalene, and methyl-*tert*-butyl-ether. The VPH method identifies all of the aromatic compounds after *o*-xylene to naphthalene. The reason for the distinction of aromatic from aliphatic compounds rests on current data, which suggests aromatic compounds are more toxic.

The FID detector is used only for reporting aliphatic compounds. This detector responds to all hydrocarbons, thereby necessitating the subtraction of aromatic and target compounds. The latter analytes subsequently are reported on the PID detector. There are two aliphatic ranges: C5 to C8, which elute from *n*-pentane to just before *n*-nonane; and C9 to C12, which elute from *n*-nonane to just before naphthalene.

### Analytical Reference Materials

Running MA VPH method requires calibrating 13 separate compounds. These 13 compounds allow for the determination of three groups of analytes in the sample: total gasoline, aliphatic and aromatic hydrocarbons, and individual target compounds. Restek offers the required mixtures with a Certificate of Analysis or with complete data packs that can be used for audits and internal quality assurance. The VPH mixtures are made in the appropriate concentrations for spiking, ensuring accurate identification and quantitation of environmental samples in your laboratory. Restek also offers high concentration mixes that can be diluted down to a spiking concentration, useful for cost savings.

## Product Listing

### Rtx<sup>®</sup>-502.2 Columns (Fused Silica)

ID	df (µm)	20m	30m	40m	60m	105m
0.18mm	1.00	40914	—	40915	—	—
0.25mm	1.40	—	10915	—	10916	—
0.32mm	1.80	—	10919	—	10920	10921
0.53mm	3.00	—	10908	—	10909	10910

### MXT<sup>®</sup>-502.2 Columns (Silcosteel<sup>®</sup>)

ID	df (µm)	30m	60m	105m
0.28mm	1.60	70919	70920	70921
0.53mm	3.00	70908	70909	70910

### MA VPH Matrix Spike Mix w/ Surrogate

benzene	<i>n</i> -pentane
ethylbenzene	toluene
isooctane	1,2,4-trimethylbenzene
2-methylpentane	<i>m</i> -xylene
methyl- <i>tert</i> -butyl-ether	<i>o</i> -xylene
naphthalene	<i>p</i> -xylene
<i>n</i> -nonane	2,5-dibromotoluene (surrogate)

2500µg/mL each in P&T methanol, 1mL/ampul.

	each	5-pack	10-pack
	30454	30454-510	
w/data pack	30454-500	30454-520	30554

### MA VPH Standard

benzene	500µg/mL	<i>n</i> -pentane	1000µg/mL
ethylbenzene	500	toluene	1500
isooctane	1500	1,2,4-trimethylbenzene	1000
2-methylpentane	1500	<i>m</i> -xylene	1000
methyl- <i>tert</i> -butyl-ether	1500	<i>o</i> -xylene	1000
naphthalene	1000	<i>p</i> -xylene	1000
<i>n</i> -nonane	1000		

in P&T methanol, 1mL/ampul.

	each	5-pack	10-pack
	30434	30434-510	
w/data pack	30434-500	30434-520	30534

### MA VPH Standard w/ Surrogate

benzene	500µg/mL	<i>n</i> -pentane	1000µg/mL
ethylbenzene	500	toluene	1500
isooctane	1500	1,2,4-trimethylbenzene	1000
2-methylpentane	1500	<i>m</i> -xylene	1000
methyl- <i>tert</i> -butyl-ether	1500	<i>o</i> -xylene	1000
naphthalene	1000	<i>p</i> -xylene	1000
<i>n</i> -nonane	1000	2,5-dibromotoluene*	1000

in P&T methanol, 1mL/ampul.

\*surrogate

	each	5-pack	10-pack
	30452	30452-510	
w/data pack	30452-500	30452-520	30552

### MA VPH Surrogate Standard

2,5-dibromotoluene

1000µg/mL in P&T methanol, 1mL/ampul.

	each	5-pack	10-pack
	30435	30435-510	
w/data pack	30435-500	30435-520	30535

10,000µg/mL in P&T methanol, 1mL/ampul.

	each	5-pack	10-pack
	30453	30453-510	
w/data pack	30453-500	30453-520	30553

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