

## Validation of New VPH GC/MS Method using Multi-Matrix Purge and Trap Sample Prep System

### Application Note

#### Abstract

The Massachusetts Department of Environmental Protection (MassDEP) developed the “Method for the Determination of Volatile Petroleum Hydrocarbons (VPH) by Gas Chromatography/Mass Spectrometry” to measure the collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in aqueous and soil/sediment matrices<sup>1</sup>.

The previous method for VPH determination required both Flame Ionization (FID) and Photoionization (PID) detectors, while this method utilizes Mass Spectrometry. This method uses Purge and Trap technology, which allows for the determination of volatile organic compounds (VOCs) at low concentration levels with precision and accuracy. The Teledyne Tekmar Atomx automated VOC sample prep system will be used to validate this method for both water and soil matrices. Calibration curves and detection limits will be established for the aliphatic and aromatic petroleum hydrocarbons listed in the MassDEP VPH method.



#### Introduction

Regulatory agencies, such as the Massachusetts DEP, develop analytical testing procedures to ensure clean air, water, and soil. Due to their potential impact on water and soil, petroleum hydrocarbon contamination from leaking underground storage tanks is a major concern. Many of these compounds, such as benzene and xylenes, have EPA-established Maximum Contaminant Levels (MCLs) due to their potential health effects<sup>2</sup>. Studies have shown that acute exposure to high levels of many of these compounds can affect the central nervous system with symptoms such as lethargy, confusion, dizziness, and nausea. Chronic effects can also include effects on the liver, kidney, blood, and nervous system. With the potential risks of exposure to volatile petroleum hydrocarbons, it is important to have methods to analyze and monitor these compounds.

The “Method for the Determination of Volatile Petroleum Hydrocarbons by Gas Chromatography” was developed by the Massachusetts DEP (MassDEP) to measure the collective concentrations of volatile aliphatic and aromatic hydrocarbons<sup>1</sup>. Originally this analysis was performed using flame ionization (FID) as the preferred detection method, but interest has grown in utilizing a mass spectrometry. Table 1 lists and categorizes the compounds to be monitored using a GC/MS. This study employs the GC conditions outlined specifically in the draft method. Further evaluation may be required, pending any changes, once the method is finalized.

Analyte	Analyte Type	Retention Time	Quantitation Ion	Confirming Ions
<b>Pentafluorobenzene</b>	<b>Internal Standard</b>	<b>5.202</b>	<b>96</b>	<b>70</b>
Methyl tertiary butyl ether	Target Analyte	3.255	73	45
n-Pentane	C <sub>5</sub> -C <sub>8</sub> Aliphatic	2.204	43	57, 72
n-Hexane	C <sub>5</sub> -C <sub>8</sub> Aliphatic	3.472	57	41, 43, 56
2,3-Dimethylpentane	C <sub>5</sub> -C <sub>8</sub> Aliphatic	5.355	56	43, 57, 41
Cyclohexane	C <sub>5</sub> -C <sub>8</sub> Aliphatic	5.743	56	84, 41
Benzene	Target Analyte	6.436	78	52, 51
n-Heptane	C <sub>5</sub> -C <sub>8</sub> Aliphatic	9.101	43	71, 57, 100
n-Octane	C <sub>5</sub> -C <sub>8</sub> Aliphatic	9.103	43	85, 57, 71
<b>Chlorobenzene-d5</b>	<b>Internal Standard</b>	<b>11.529</b>	<b>117</b>	<b>119, 82</b>
Toluene	Target Analyte	9.403	91	92
<b>Toluene-D8</b>	<b>Surrogate Standard</b>	<b>9.279</b>	<b>98</b>	<b>100, 42</b>
Ethylbenzene	Target Analyte	11.672	91	106
m,p-Xylene	Target Analyte	11.784	91	106, 105
o-Xylene	Target Analyte	12.409	91	106, 105
<b>1,4-Dichlorobenzene-d4</b>	<b>Internal Standard</b>	<b>14.586</b>	<b>152</b>	<b>115, 150</b>
2,3-Dimethylheptane	C <sub>9</sub> -C <sub>12</sub> Aliphatic	10.506	43	84, 85
n-Nonane	C <sub>9</sub> -C <sub>12</sub> Aliphatic	11.422	43	57, 85
Isopropylbenzene	C <sub>9</sub> -C <sub>10</sub> Aromatic	12.906	105	120
n-Decane	C <sub>9</sub> -C <sub>12</sub> Aliphatic	13.289	57	43, 71, 85
1-Methyl-3-ethylbenzene	C <sub>9</sub> -C <sub>10</sub> Aromatic	13.535	105	120
1,3,5-Trimethylbenzene	C <sub>9</sub> -C <sub>10</sub> Aromatic	13.605	105	120
Butylcyclohexane	C <sub>9</sub> -C <sub>12</sub> Aliphatic	14.168	83	55, 82
p-isopropyltoluene	C <sub>9</sub> -C <sub>10</sub> Aromatic	14.407	119	105, 134
1,2,3-Trimethylbenzene	C <sub>9</sub> -C <sub>10</sub> Aromatic	14.581	105	120
n-Undecane	C <sub>9</sub> -C <sub>12</sub> Aliphatic	14.646	57	43, 71, 85
n-Dodecane	C <sub>9</sub> -C <sub>12</sub> Aliphatic	15.727	57	43, 71, 85
Naphthalene	Target Analyte	16.827	128	

Table 1: MassDEP Volatile Petroleum Hydrocarbon Analytes

This method has been designed to complement the toxicological approach to evaluate human health effects that may result from exposure to petroleum hydrocarbons. Table 2 lists the current Massachusetts regulatory limit on petroleum hydrocarbons.

Current Massachusetts Regulatory Limit	
C <sub>5</sub> -C <sub>8</sub> Aliphatic	0.3 mg/L
C <sub>9</sub> -C <sub>12</sub> Aliphatic	0.7 mg/L
C <sub>9</sub> -C <sub>10</sub> Aromatic	0.2 mg/L

Table 2: Current Massachusetts Regulatory Limits for Petroleum Hydrocarbons

These regulatory limits require instrumentation capable of analysis at low concentrations. Purge and Trap technology allows for the determination VOCs at these low levels with precision and accuracy. This study will employ a Teledyne Tekmar Atomx automated VOC sample prep system to validate the MassDEP GC-MS VPH method for both water and soil matrices. Soil samples are analyzed utilizing automated methanol extraction, exclusive to the Atomx, and quantified using a water-based calibration.

### **Experimental-Instrument Conditions**

An Agilent 7890A GC and 5975C inert XL MSD with Triple Axis Detector (TAD) was used in this study. Tables 3 and 4 list the GC/MS conditions. An Atomx automated VOC sample prep system was employed using the purge and trap parameters outlined in Table 5 and a #9 analytical trap.

GC Parameters	
GC:	Agilent 7890A
Column	Restek RTX-502.2 30m x 0.25 mmID x 1.4 µm
Oven Program:	50 °C for 5 min; 11 °C/min to 130 °C for 0 min; 20 °C /min to 250 °C for 1 min
Inlet:	240 °C
Column Flow	1.0 mL/min
Gas:	Helium
Split:	50:1
Pressure:	12.401 psi
Inlet:	Split

MSD Parameters	
MSD:	5975C inert XL with TAD
Source:	250 °C
Quad:	200 °C
Solvent Delay:	0.5 min
Scan Range:	m/z 35-250
Scans:	5.19 scans/sec
Threshold:	150
MS Transfer Line Temp:	250 °C

Tables 3 and 4: GC and MSD Parameters

Atomx Water Parameters			
Variable	Value	Variable	Value
Valve oven Temp	140 °C	Dry Purge Flow	100 mL/min
Transfer Line Temp	140 °C	Dry Purge Temp	20 °C
Sample Mount Temp	90 °C	Methanol Needle Rinse	Off
Water Heater Temp	90 °C	Methanol Needle Rinse Volume	3.0 mL
Sample Vial Temp	20 °C	Water Needle Rinse Volume	7.0 mL
Sample Equilibrate Time	0.00 min	Sweep Needle Time	0.25 min
Soil Valve Temp	40 °C	Desorb Preheat Time	245 °C
Standby Flow	10 mL/min	GC Start Signal	Start of Desorb
Purge Ready Temp	40 °C	Desorb Time	2.00 min
Condensate Ready Temp	45 °C	Drain Flow	300 mL/min
Presweep Time	0.25 min	Desorb Temp	250 °C
Prime Sample Fill Volume	3.0 mL	Methanol Glass rinse	On
Sample Volume	5.0 mL	Number of Methanol Glass Rinses	1
Sweep Sample Time	0.25 min	Methanol Glass Rinse Volume	7.0 mL
Sweep Sample Flow	100 mL/min	Number of Bake Rinses	1
Sparger Vessel Heater	Off	Water Bake Rinse Volume	7.0 mL
Sparge Vessel Temp	20 °C	Bake Rinse Sweep Time	0.25 min
Prepurge Time	0.00 min	Bake Rinse Sweep Flow	100 mL/min
Prepurge Flow	0 mL/min	Bake Rinse Drain Time	0.40 min
Purge Time	11.00 min	Bake Time	7.00 min
Purge Flow	40 mL/min	Bake Flow	200 mL/min
Purge Temp	20 °C	Bake Temp	280 °C
Condensate Purge Temp	20 °C	Condensate Bake Temp	200 °C
Dry Purge Time	0.00 min		

Table 5: Atomx Parameters (parameters highlighted in yellow were not used.)

## **Calibration Data and Method Detection Limits**

A stock solution in was prepared at 100 ppm in methanol. From this stock, an eight-point calibration from 1-200 ppb was prepared. According to this MassDEP VPH method, evaluation using Relative Response Factors (RRFs) is preferred, but linear regression is permissible. For this study, linear regressions were used to evaluate the data and determine the Method Detection Limit (MDL). Agilent ChemStation software was used to process the calibration data.

Figure 1 is a total ion chromatogram (TIC) of a 10 ppb VPH standard. Figure 2 shows the calibration curve for ethylbenzene, a target analyte from the MassDEP VPH method, as an example. According to the method, a passing calibration has a linear regression factor of 0.995 or greater. Calibration data and MDLs for all compounds can be found in Table 6.

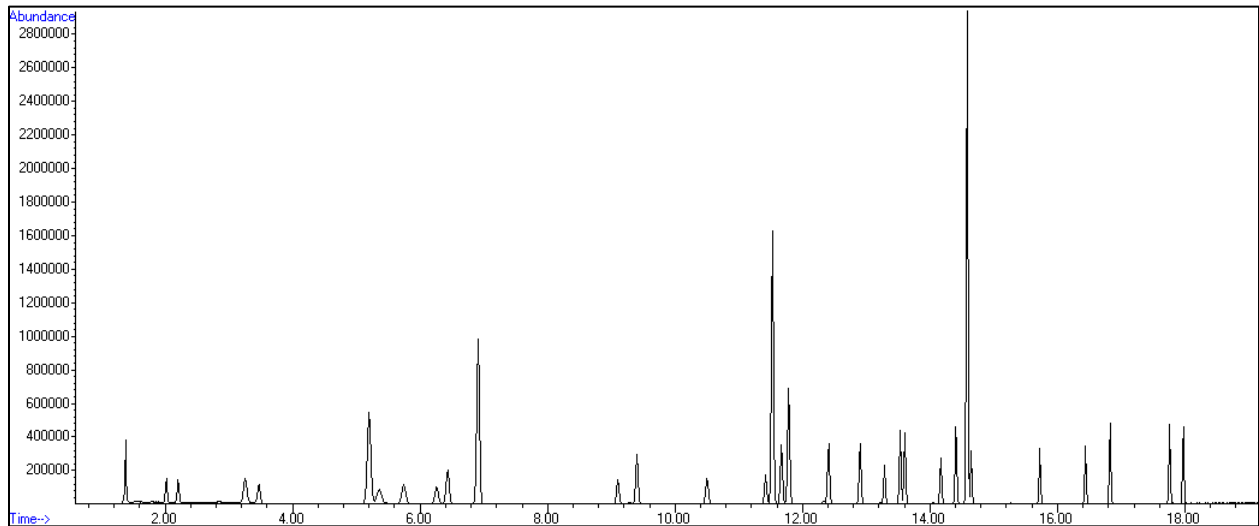


Figure 1: Chromatogram of a 10 ppb standard for MassDEP VPH by GC/MS method.

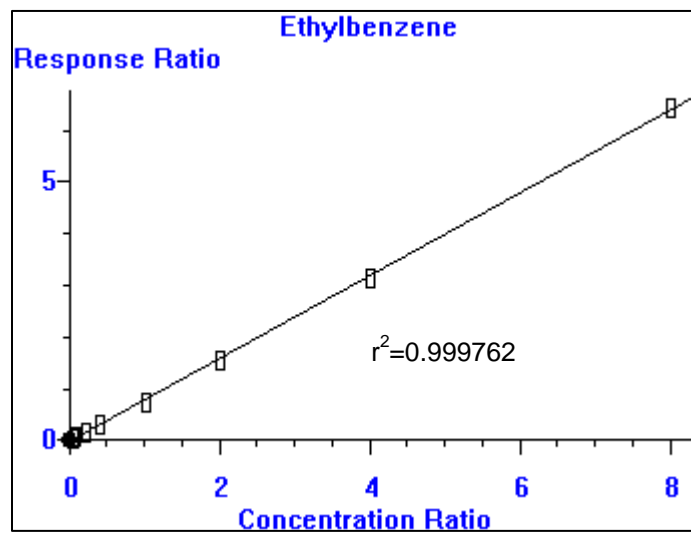


Figure 2: Calibration curve for Ethylbenzene, a target analyte for the VPH by GC/MS method.

Analyte Group	Linear Regression Factor (r <sup>2</sup> )	MDL*
<b>Total C5-C8 Aliphatic</b>	0.9965	0.23
<b>Total C9-C12 Aliphatic</b>	0.9982	0.20
<b>Total C9-C10 Aromatic</b>	0.9965	0.20
<b>Target Analytes</b>		
Methyl Tert-butyl Ether	0.9997	0.18
Benzene	0.9994	0.11
Toluene	0.9993	0.15
Ethylbenzene	0.9998	0.12
m,p-Xylenes	0.9993	0.11
o-Xylene	0.9992	0.12
Naphthalene	0.9987	0.07

Table 6: Calibration and MDL Results for MassDEP VPH Analytes (\*Analysis at 2 ppb, n=7)

The Minimum Detection Limits (MDL) for this study were determined by analyzing seven samples at 2 ppb and using the equation below to obtain a value.

$$\text{MDL} = (\text{Standard Deviation}) * (\text{Student's } t \text{ value for 99\% confidence level})$$

$$T \text{ value for 7 replicates} = 3.14$$

## Conclusions

Studies have shown that exposure to high levels of petroleum hydrocarbons can have negative effects on human health. With these implications in mind, it is important to have a method to detect these compounds at low levels. The Massachusetts Department of Environmental Protection developed a method to measure volatile petroleum hydrocarbons using FID.

Using Teledyne Tekmar's Atomx automated VOC sample prep system, the MassDEP VPH method has been successfully validated using GC/MS. Due to the draft status of this method, further evaluation may be required once it has been finalized. Calibration criteria of this method were met, with linear regression values greater than 0.995 for all compounds. Using the Atomx's automated methanol extraction for soil samples can also lead to considerable time savings.

## References

- 1) Method for the Determination of Volatile Petroleum Hydrocarbons (VPH) by Gas Chromatography/Mass Spectrometry, Massachusetts Department of Environmental Protection, February 2012.
- 2) Drinking Water Contaminants, United States Environmental Protection Agency, <http://water.epa.gov/drink/contaminants/index.cfm>