Determination of Volatile Petroleum Hydrocarbons

ANNE JUREK

Abstract:

Due to current events, the importance of determining volatile petroleum hydrocarbons in both soils and waters has become an issue. The complexities of the matrices that these compounds are found in can also inhibit accurate detection. Analysis of volatile petroleum hydrocarbons by purge and trap concentration in conjunction with GC/MS will be presented in this poster.

Discussion:

The analysis of Volatile Petroleum Hydrocarbons (VPH) requires purge and trap concentration in tandem with a Gas Chromatograph (GC) for compound separation. For compound determination, a Flame Ionization Detector and a Photoionization Detector (FID/PID) are used in series. Finally, a Mass Spectrometer (MS) is also an option for confirmatory analysis. The method is employed for the analysis of ground water, soils and/or any other solid waste that can be extracted in methanol.

There are many issues with this method that can cause problems with the analysis. Firstly, the method requires a four minute desorb time which causes a rise in the baseline due to moisture being delivered to the GC along with the analytes. Furthermore, many of the samples for this analysis are soils and/or sediments. Since these matrices need to be extracted in methanol, there is the added concern of the methanol extract in the sample causing co-elution issues.

EST Analytical developed a unique Desorb Flow Control (DFC) feature for the Encon Evolution that will help to control the moisture and methanol complications that are seen during the required four minute desorb of the VPH method. DFC (patent pending) is a feature that allows the user the ability to control the flow to the GC inlet independent of the split ratio during desorb. During the desorb step, all of the analytes are desorbed during the first half minute, the other three and a half minutes allow more water to be delivered to the GC. DFC allows the analyst to change the split rate at any given time during the desorb step. Thus, a 5:1 split can be used during the first half minute of the desorb time allowing for better analyte recovery. After the initial half minute, the Evolution can add flow to the GC inlet at a rate of 135ml/min effectively changing the split rate to 140:1 for the last three and a half minutes of the desorb step.

Experimental:

The VPH method requires the use of a water sampling system as the matrices are water or methanol extractions, thus the Centurion W was used for the autosampler. The concentrator utilized was the Encon Evolution configured with a K Trap. An Agilent 6890 GC configured with a Restek Rtx-502.2 60m x 0.25mm I.D. x 1.4µm column was used for analyte separation and an Agilent 5973 MS for data analysis. The MS was used in order to highlight the DFC's ability to control moisture during the 4 minute desorb process. Purge and Trap and GC/MS parameters are listed in Tables 1 and 2 respectively.

Purge and Trap Concentrator	**EST Encon Evolution**
Trap Type	Vocarb 3000 (K)
Valve Oven Temp.	150ºC
Transfer Line Temp.	150ºC
Trap Temp.	35ºC
Moisture Reduction Trap (MoRT) Temp.	39ºC
Purge Time	11 min.
Purge Flow	40mL/min
Dry Purge Temp.	ambient
Dry Purge Flow	40mL/min
Dry Purge Time	2.0 min.
Desorb Flow Control	On (Program)
Desorb Pressure Control	On
Desorb Pressure	14psi
Desorb Time	4.0 min.
Desorb Preheat Delay	10 sec.
Desorb Temp.	260ºC
Moisture Reduction Trap (MoRT) Bake Temp.	200ºC
Bake Temp	265ºC
Sparge Vessel Bake Temp.	110ºC
Bake Time	8 min.
Bake Flow	85mL/min
Purge and Trap Auto-Sampler	**EST Centurion WS**
Sample Size	5mL
Internal Standard Volume	NA
Desorb Flow Control Program:	**EST Encon Evolution**
Enable Ramp Control	On
Initial Pressure	20.8psi
Initial Hold Time	0.3min
Ramp Rate	25psi/min
Final Pressure	31psi

Table 1: Purge and Trap Parameters

GC/MS	Agilent 6890/5973
Inlet	Split/Splitless
Inlet Temp.	200ºC
Inlet Head Pressure	20.34 psi
Mode	Split
Split Ratio	5:1
Column	Rtx-502.2 60m x 0.25mm I.D. 1.4µm film thickness
Oven Temp. Program	45ºC hold for 1 min., ramp 5ºC/min to 100ºC, ramp 12ºC/min to 240ºC, hold for 4.33min, 28min run time.
Column Flow Rate	1.0mL/min
Gas	Helium
Total Flow	42.0mL/min
Source Temp.	230ºC
Quad Temp.	150ºC
MS Transfer Line Temp.	180ºC
Scan Range	m/z 30-265
Scans	3.06 scans/sec
Solvent Delay	3.0 min

Table 2: GC/MS Parameters

The 16 component Massachusetts VPH standard with Surrogate was obtained from Restek at a concentration of 10,000µg/ml. 20ppb calibration standards were prepared as water samples and with additional methanol in order to mimic a methanol extract. These standards were run on the purge and trap concentrator. The purge and trap experimental parameters were altered in order to assess the effect DFC has on the raised baseline caused by moisture transfer and also the methanol/n-Pentane co-elution issues when running methanol extracts, see Table 3.

Experiment	Methanol Added	DFC	0.5 minute Desorb	4 minute desorb
1	No	Yes	No	Yes
2	No	No	No	Yes
3	No	No	Yes	No
4	Yes	Yes	No	Yes
5	Yes	No	No	Yes
6	Yes	No	Yes	No

Table 3: Summary of Experimental Parameters Evaluated

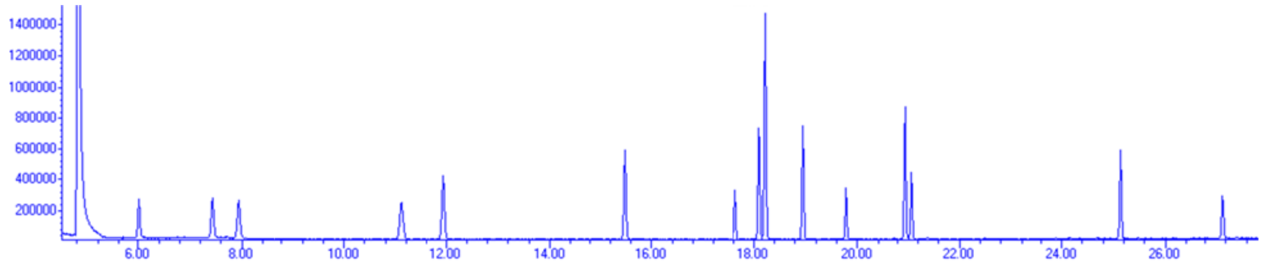

Figure 1: Experiment 1

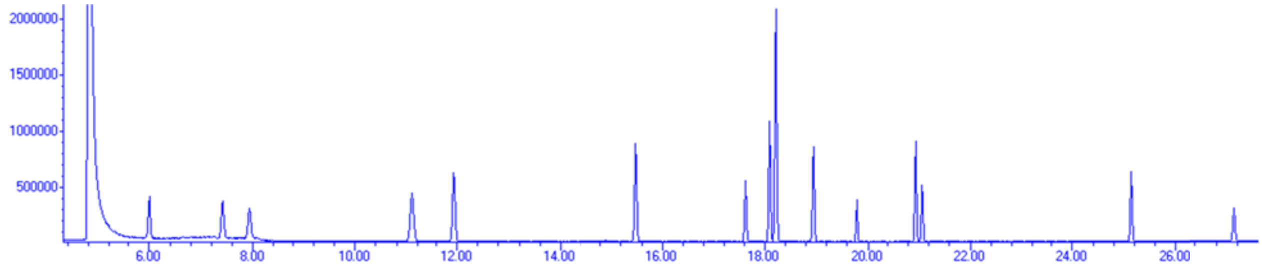

Figure 2: Experiment 2

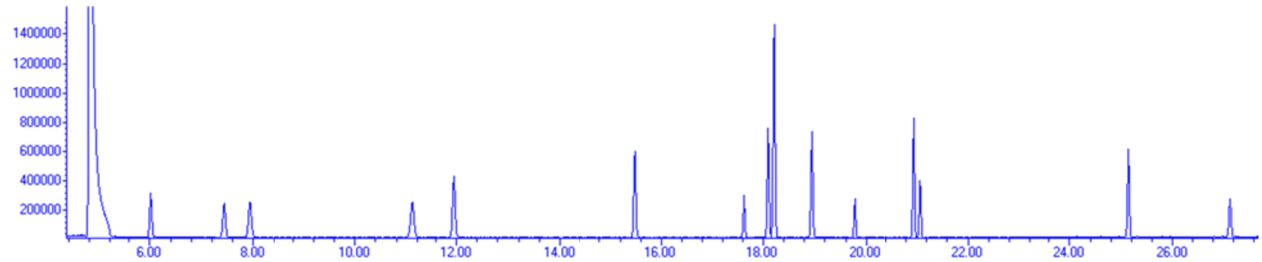

Figure 3: Experiment 3

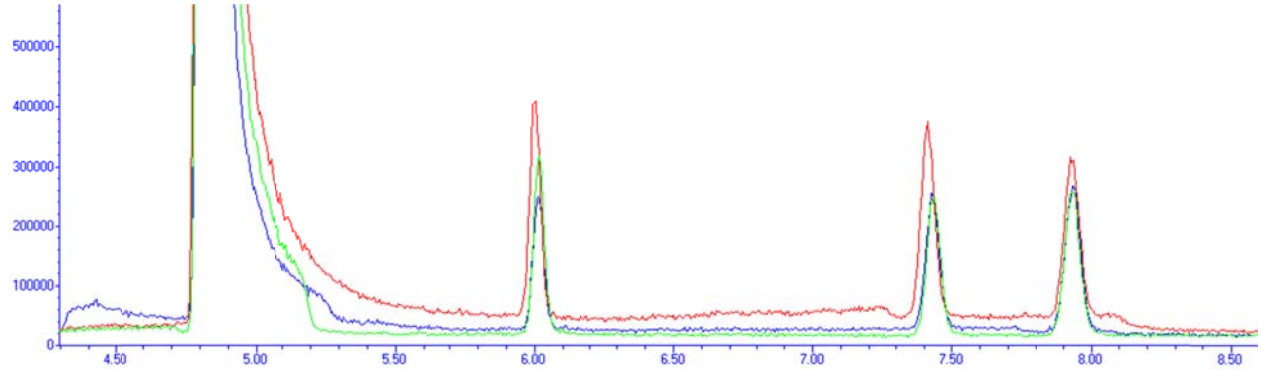

Figure 4: Overlay Displaying Moisture Control and Peak Separation of Experiments 1 (blue), 2 (red), and 3 (green)

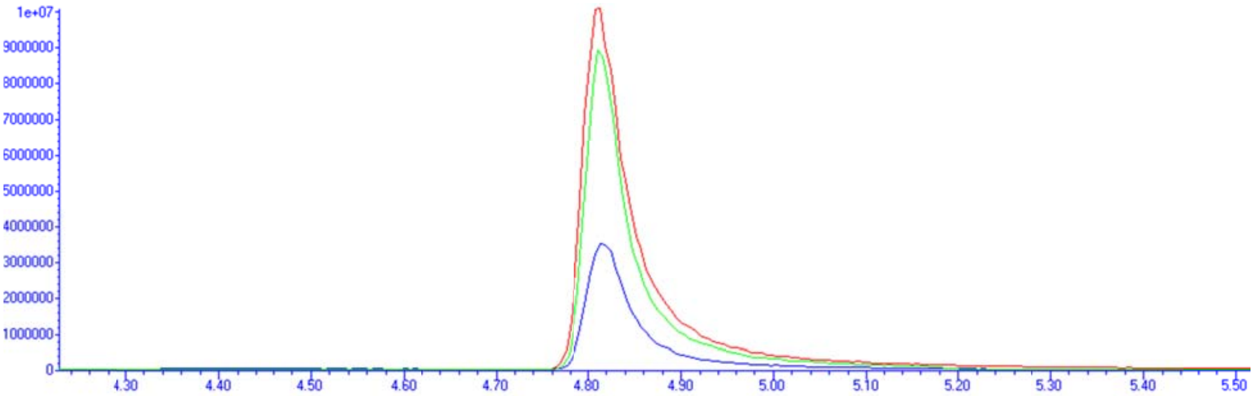

Figure 5: Overlay of Methanol Peak Seen in Experiments 1 (blue), 2 (red), and 3 (green)

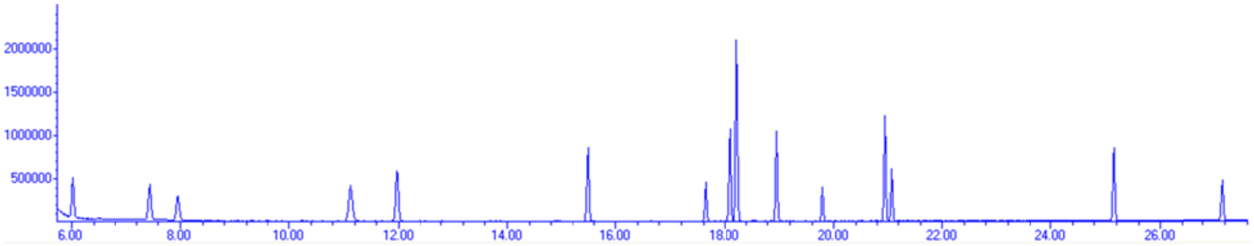

Figure 6: Experiment 4

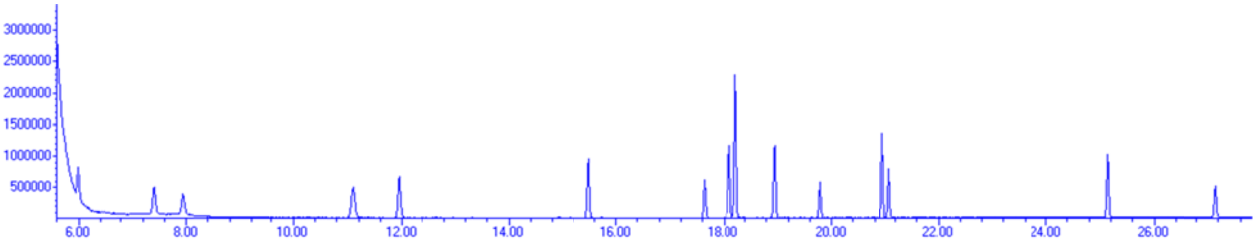

Figure 7: Experiment 5

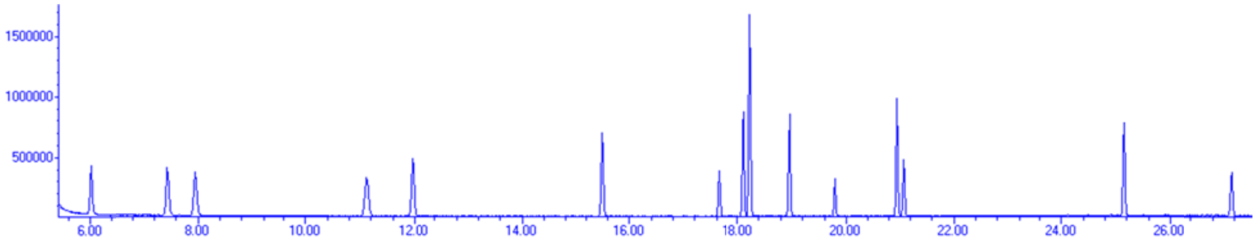

Figure 8: Experiment 6

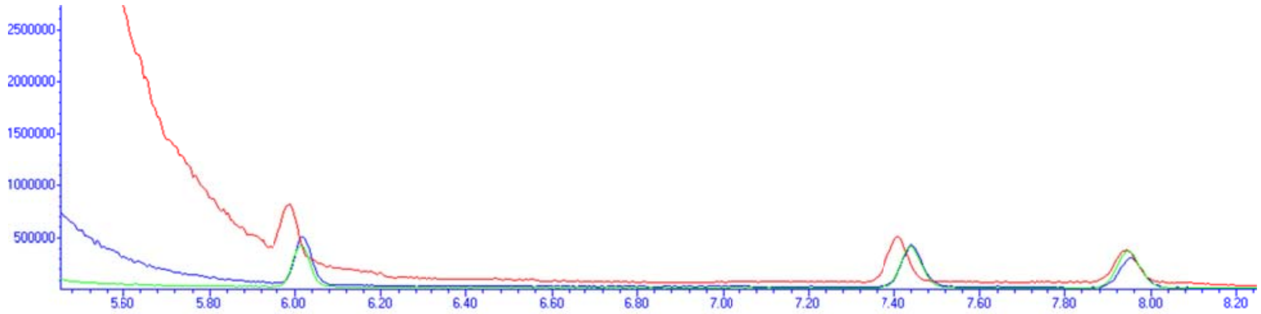

Figure 9: Overlay Displaying Moisture Control and Peak Separation of Experiments 4 (blue), 5 (red), and 6 (green)

Conclusion:

The Massachusetts VPH method is a valuable tool for the determination of Volatile Petroleum Hydrocarbons. However, the 4 minute desorb time is a problematic requirement of this method as it causes moisture and co-elution issues. The Encon Evolution with Desorb Flow Control did an exceptional job at controlling the amount of moisture transferred to the GC during the 4 minute desorb step required by the method. The chromatography displayed that DFC was able to limit moisture and co-elution issues seen with this method about as well as a 30 second desorb time. DFC also has the added advantage of controlling methanol transfer and reducing overall helium consumption.

References:

1. Method for the Determination of Volatile Petroleum Hydrocarbons, Massachusetts Department of Environmental Protection, Revision 1.1, May 2004.