Determining Volatile Organic Compounds from Difficult Soil Matrices Utilizing Both Headspace and Purge and Trap Techniques

Abstract

Purge and Trap concentration (P&T) along with Gas Chromatography/Mass Spectrometry (GC/MS) analysis is the traditionally used method for the analysis of Volatile Organic Compounds (VOCs). This application note investigates P&T concentration of VOCs in soils utilizing both the standard soil and the automated methanol extraction technique of Teledyne Tekmar's Atomx, a combination P&T concentrator and multimatrix autosampler system. Furthermore, we will demonstrate an alternative method for the analysis of VOCs in soils utilizing both the Static and Dynamic modes of Teledyne Tekmar's HT3™ Automated Headspace Analyzer. The analysis of soils presents several challenges as the composition of the soil matrix can vary. Thus, this application note will also inquire into different soil matrices and how to best determine the VOCs present in them.

Introduction

The potential for soils to be contaminated with VOCs can be quite high especially if the soil sample is near a commercial area, a landfill, a manufacturing facility or a host of other potentially contaminated sites. The amount of contamination can vary from parts per billion (ppb) to pure product contamination. The type of soil being contaminated can also vary from sand, to clay, to a humic soil. In order to analyze VOCs in a soil matrix it becomes necessary to account for all of these variances.

In this study, sand, clay and humic soil were analyzed via P&T concentration, utilizing the Atomx, and by Headspace analysis, using the HT3™ Automated Headspace Analyzer. The results of these analyses were then compared in order to show the benefits and the possible problems with these analyses and their respective levels of detection. From these examinations, experimental and instrumental conditions were optimized and recommendations on the type of analysis that would best suit the level of contamination and the type of soil matrix being examined.

Definitions

1. Static Headspace

A soil sample is placed in a sealed vial and thermostatically controlled for a fixed amount of time. Once equilibration is achieved between the sample and gaseous phases a sample of the gas phase is introduced to the GC/MS for separation, identification, and quantification.

2. Dynamic Headspace

The same procedure as Static is employed with the exception being the vial is not permitted to reach equilibrium and instead the headspace is continually swept onto an adsorbent trap where the compounds of interest are concentrated. After a certain amount of time the adsorbent trap is heated and back flushed to the GC/MS.

3. In Vial Purge

A soil sample is placed in a sealed vial containing a predetermined amount of laboratory grade water and a magnetic mixing bar. An inert purge gas is introduced directly into the soil water slurry while the sample is mixing via a two stage sampling needle. The purge gas exits the vial extracting the compounds of interest and depositing them onto an adsorbent trap. Then as in Dynamic Headspace the analytical trap is heated and back flushed to the GC/MS.

4. Solvent Extraction

A soil sample is placed in a vial containing a predetermined amount of solvent and mixed for a fixed amount of time. Once the compounds have diffused from the soil and into the solvent, an aliquot of the extract is transferred into laboratory grade water. The water and extract are then purged similarly as to the In Vial Purge with the difference being they are placed in a fritted glass sparger that increases surface interaction via the frit which finely divides the incoming purge gas. Desorption and transfer to the GC/MS is the same as the previously mentioned three techniques.

Experimental-Instrument Conditions

The Atomx P&T Concentrator/Multimatrix Autosampler and the HT3™ Automated Headspace Analyzer were coupled to an Agilent 7890A GC and a 5975C inert XL MSD for these analyses. The Atomx and the HT3™ were both equipped with a #9 adsorbent trap. Tables 1 and 2 display the GC, MSD conditions while Tables 3 and 4 display the Atomx conditions for low and high level VOC analysis. The HT3™ Automated Headspace Analyzer Static and Dynamic experimental conditions are listed in Tables 5 and 6 respectively.

GC Parameters	
GC:	Agilent 7890A
Column:	J&W Scientific DB-VRX 30m x 0.250mm x1.4um
Oven Program:	35°C for 4 min; 16°C/min to 85°C for 0 min; 30°C /min to 210°C for 3 min, 14.29 min runtime
Inlet:	220°C
Column Flow	1.2mL/min
Gas:	Helium
Split:	80:1
Pressure:	9.3 psi
Inlet:	Split/Splitless

MSD Parameters	
MSD:	5975C Inert XL
Source:	230°C
Quad:	150°C
Solvent Delay:	0.5 min
Scan Range:	m/z 35-300
Scans:	4.51 scans/sec
Threshold:	400
MS Transfer Line Temp:	230°C

Tables 1 & 2: GC and MSD Parameters

Atomx Solvent Extraction Parameters			
Variable	Value	Variable	Value
Valve Oven Temp	140°C	Dry Purge Flow	100mL/min
Transfer Line Temp	140°C	Dry Purge Temp	20°C
Sample Mount Temp	90°C	Methanol Needle Rinse	On
Water Heater Temp	90°C	Methanol Needle Rinse Volume	Varied
Soil Valve Temp	100°C	Water Needle Rinse Volume	7.0mL
Standby Flow	10mL/ min	Sweep Needle Time	Varied
Purge Ready Temp	40°C	Desorb Preheat Temp	245°C
Condensate Trap Standby	45°C	GC Start Signal	Start of Desorb
Presweep Time	0.25 min	Desorb Time	2.00 min
Methanol Volume	0.0mL	Drain Flow	300mL/min
Sparge Vessel Heater	Off	Desorb Temp	250°C
Sparge Vessel Temp	20°C	Methanol Glass Rinse	On
Prepurge Time	0.00 min	Number of Methanol Glass Rinses	1
Prepurge Flow	0mL/min	Methanol Glass Rinse Volume	3.0mL
Sample Mix Speed	Varied	Number Of Bake Rinses	1
Sample Mix Time	Varied	Water Bake Rinse Volume	7.0mL
Sample Mix Settle Time	Varied	Bake Rinse Sweep Time	0.25 min
Sample Sweep Time	0.25 min	Bake Rinse Sweep Flow	100mL/min
Sample Sweep Flow	100mL/min	Bake Rinse Drain Time	0.40 min
Purge Time	11.00 min	Bake Time	4.00 min
Purge Flow	40mL/min	Bake Flow	250mL/min
Purge Temp	20°C	Bake Temp	280°C
Condensate Purge Temp	20°C	Condensate Bake Temp	200°C
Dry Purge Time	1.00 min		

Table 3: Atomx High Level, Solvent Extraction, VOC Parameters (Parameters highlighted in yellow were varied and dependant on the soil matrix.)

Atomx Low Level Soil Parameters			
Variable	Value	Variable	Value
Valve Oven Temp	140°C	Purge Time	11.0 min
Transfer Line Temp	140°C	Purge Flow	40mL/min
Sample Mount Temp	90°C	Purge Temp	20°C
Water Heater Temp	90°C	Condensate Purge Temp	20°C
Sample Vial Temp	40°C	Dry Purge Time	2.00 min
Prepurge Time	0.00 min	Dry Purge Flow	100mL/ min
Prepurge Flow	0mL/min	Dry Purge Temp	20°C
Preheat Mix Speed	Slow	Methanol Needle Rinse	On
Sample Preheat Time	0.00 min	Methanol Needle Rinse Volume	Varied
Soil Valve Temp	100°C	Water Needle Rinse Volume	7.0mL
Standby Flow	10mL/min	Sweep Needle Time	Varied
Purge Ready Temp	40°C	Desorb Preheat Temp	245°C
Condensate Temp Standby	45°C	GC Start Signal	Start of Desorb
Presweep Time	0.25 min	Desorb Time	2.00 min
Water Volume	Varied	Drain Flow	300mL/min
Sweep Water Time	0.25 min	Desorb Temp	250°C
Sweep Water Flow	100mL/min	Bake Time	4.00 min
Sparge Vessel Heater	Off	Bake Flow	250mL/min
Sparge Vessel Temp	20°C	Bake Temp	280°C
Purge Mix Speed	Varied	Condensate Bake Temp	200°C

Table 4: Atomx Low Level VOC Parameters (Parameters highlighted in yellow were varied and dependant on the soil matrix.)

HT3 Static Parameters			
Variable	Value	Variable	Value
Constant Heat Time	On	Mixing Time	Varied
G.C. Cycle Time	30.00 min	Mixing Level	Varied
Valve Oven Temp	125°C	Mixer Stabilize Time	0.50 min
Transfer Line Temp	125°C	Pressurize	Varied
Standby Flow Rate	50mL/min	Pressurize Time	1.50 min
Platen/Sample Temp	Varied	Pressurize Equil. Time	0.50 min
Platen Temp Equil. Time	1.00 min	Loop Fill Pressure	Varied
Sample Equil. Time	Varied	Loop Fill Time	0.50 min
Mixer	On	Inject Time	1.00 min

Table 5: HT3™ Static Headspace Parameters (Parameters highlighted in yellow were varied and dependant on the soil matrix.)

HT3 Dynamic Parameters			
Variable	Value	Variable	Value
Valve Oven Temp	125°C	Sweep Flow Rate	Varied
Transfer Line Temp	125°C	Sweep Flow Time	Varied
Standby Flow Rate	40mL/min	Dry Purge Time	Varied
Trap Standby Temp	30°C	Dry Purge Flow	100mL/min
Trap Sweep Temp	0°C	Dry Purge Temp	25°C
Platen/Sample Temp	Varied	Desorb Preheat	255°C
Sample Preheat Time	20.00 min	Desorb Temp	260°C
Preheat Mixer	On	Desorb Time	2.00 min
Preheat Mixing Level	Varied	Trap Bake Temp	300°C
Preheat Mixing Time	Varied	Trap Bake Time	5.00 min
Preheat Mixer Stabilize Time	0.50 min	Trap Bake Flow	450mL/min

Table 6: HT3™ Dynamic Headspace Parameters (Parameters highlighted in yellow were varied and dependant on the soil matrix.)

Calibration

A 50ppb working calibration stock standard was prepared in methanol. The low level soil curve range for the in vial purge analysis utilizing Purge and Trap was 1.0-200ppb. Solvent extraction was used for the high level soil curve. The range for the solvent extraction curve was also 1.0-200ppb as the samples are at a 100 times dilution. The static headspace curve had a range of 50ppb-2.0ppm and the dynamic headspace curve range was 5.0ppb-200ppb. All of the calibration data was analyzed using Agilent Chemstation software.

Results

Sand Matrix

Baked sand was used for the sand matrix. There were a few advantages to the sand matrix the first being that the VOCs extracted into the solvent very well when using the P&T solvent extraction technique. Second most of the VOCs purged out of the sand during the in vial purge of the low level P&T analysis. Finally, most of the VOCs swept into headspace well during static and dynamic headspace analysis however, de-ionized water needed to be added to the matrix in order to better release the compounds into the headspace. The main disadvantage of the sand matrix was the interaction of the polar VOCs with the sand. These interactions caused inconsistent recoveries of these compounds during both static and dynamic headspace analysis, see figures 1 and 2. In addition, compounds with higher boiling points showed less recoveries when compared with the aqueous standard for the in vial purge as seen in figure 3. Solvent extraction, however, exhibited no issues with any of the VOCs and gave consistent recoveries for all of the compounds analyzed, see figure 4.

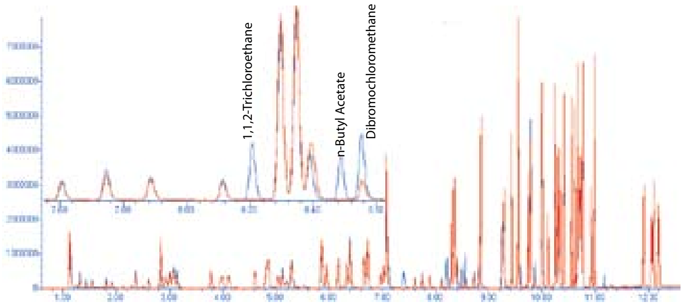

Figure 1: Overlay of 1ppm Static Headspace Sand Matrix Sample (red) and Static Headspace VOC Cal Standard (blue)

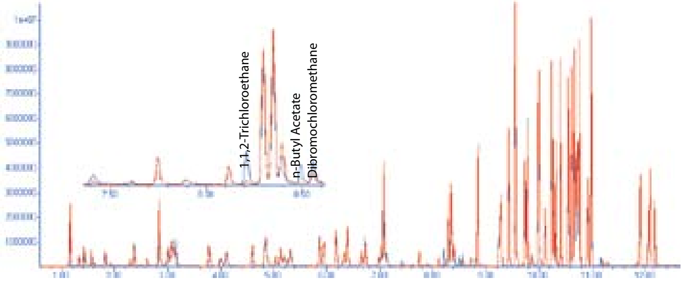

Figure 2: Overlay of 100ppb Dynamic Headspace Sand Matrix (red) Sample and Dynamic Headspace VOC Cal Standard (blue)

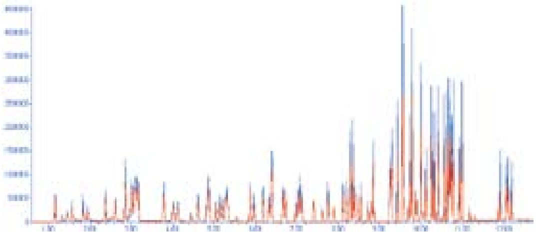

Figure 3: 50ppb Chromatogram Overlay of Low VOC Sand (red) and Low VOC Cal Standard (blue)

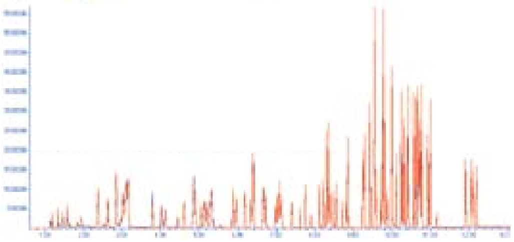

Figure 4: 50ppb Chromatogram Overlay of Solvent Extracted VOC Sand (red) and High VOC Cal Standard (blue)

Clay Matrix

Natural clay was used for the clay matrix. The clay matrix proved to have several advantages. The VOCs went into headspace very well with the addition of de-ionized water. However, due to some breakthrough, there was some loss of compound recovery with the lighter compounds, see figures 5 and 6. In addition, the VOCs extracted well for both the low level, in vial purge, and high level, solvent extraction, P&T analyses with no loss of the lighter VOCs, see figures 7 and 8. The central drawback for extracting VOCs out of a clay matrix for both headspace and P&T analyses was the longer agitation times and more vigorous mixing required for compound extraction.

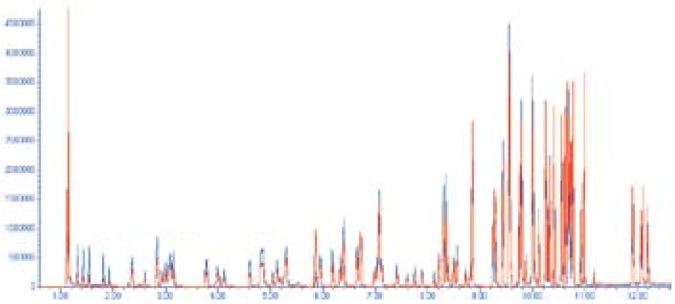

Figure 5: Overlay of 1ppm Static Headspace Clay Matrix Sample (red) and Static Headspace VOC Cal Standard (blue)

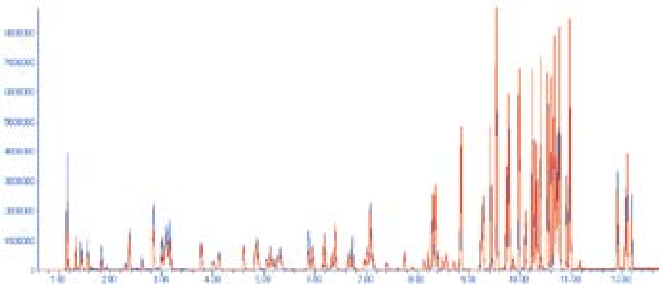

Figure 6: Overlay of 100ppb Dynamic Headspace Clay Matrix (red) Sample and Dynamic Headspace VOC Cal Standard (blue)

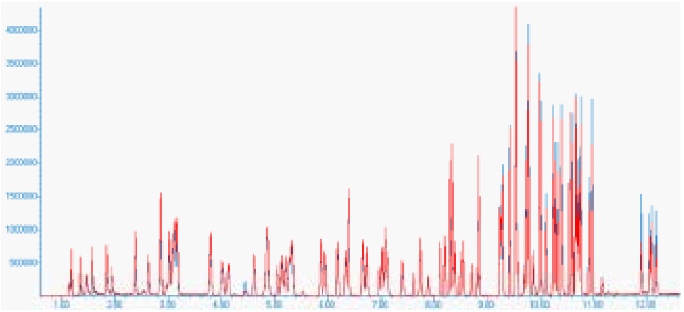

Figure 7: 50ppb Chromatogram Overlay of Low VOC Clay (red) and Low VOC Cal Standard (blue)

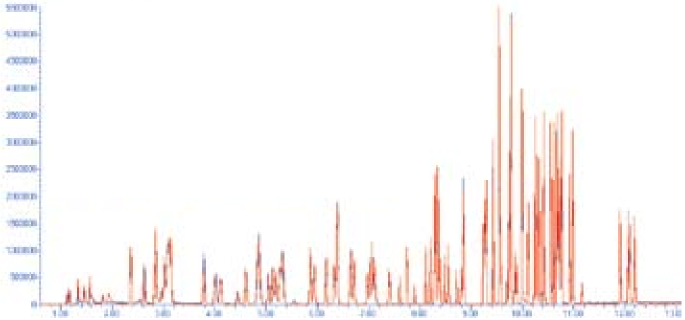

Figure 8: 50ppb Chromatogram Overlay of Solvent Extracted VOC Clay (red) and High VOC Cal Standard (blue)

Soil Matrix

Humic soil was used for the soil matrix. The humic soil was very absorbent and proved to be the most difficult matrix to extract VOCs from. The only advantage to this matrix is that the VOCs extracted into solvent very well and proved to have consistent recoveries, see Figure 12. However, there were several disadvantages to this matrix. First of all, the soil readily absorbed both de-ionized water and solvent, so all of the samples needed to be diluted further than the sand and clay matrices. Secondly, since the soil was light and did not settle well after mixing, the settle times and the sweep times had to be increased in order to achieve better VOC recoveries. In the case of P&T, a longer time was required to sweep the needle along with a larger solvent rinse of the needle in order to ensure system cleanliness. Finally, the matrix interfered with the heavier VOCs migration into headspace, see figures 9 and 10, and the purge efficiency of the heavier compounds for low level VOC P&T, see figure 11. Thus, the recoveries for the heavier VOCs were inconsistent for all of the analyses with the exception being solvent extraction.

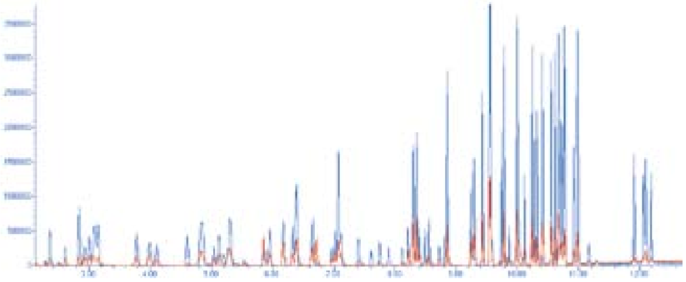

Figure 9: Overlay of 1ppm Static Headspace Soil Matrix (red) and Static Headspace VOC Cal Standard (blue)

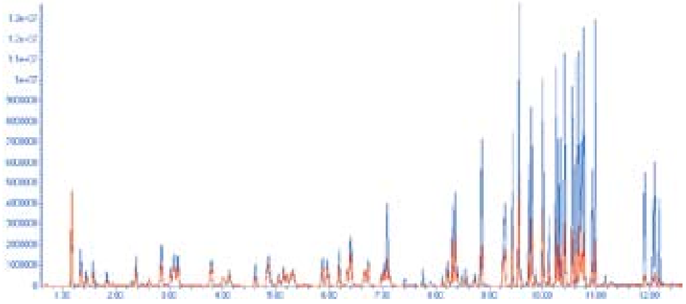

Figure 10: Overlay of 100ppb Dynamic Headspace Soil Matrix (red) Sample and Dynamic Headspace VOC Cal Standard (blue)

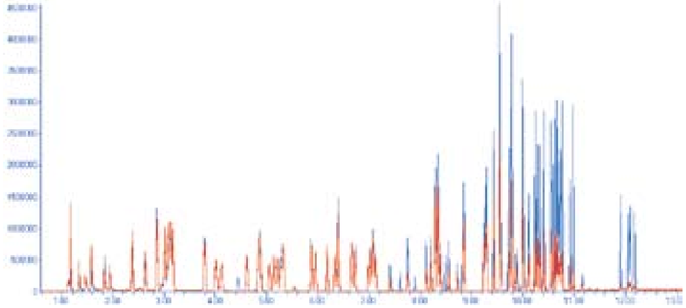

Figure 11: 50ppb Chromatogram Overlay of Low VOC Soil (red) and Low VOC Cal Standard (blue)

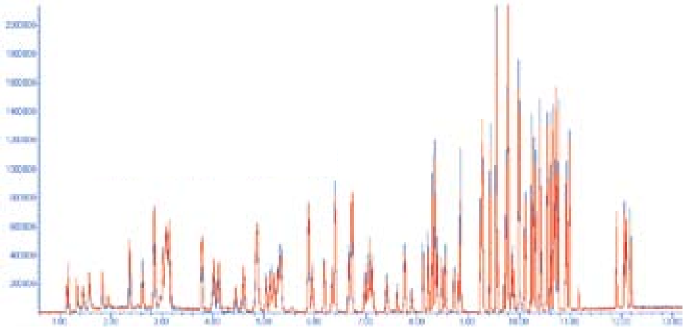

Figure 12: 50ppb Chromatogram Overlay of Solvent Extracted VOC Soil (red) and High VOC Cal Standard (blue)

Conclusions

The HT3™ Automated Headspace Analyzer offered several advantages in measuring VOCs in a soil matrix. The system can measure both high amounts of contamination utilizing the Static Headspace option and low amounts of contamination using the Dynamic Headspace option. The system also has the advantage of measuring high amounts of VOCs utilizing the Static Headspace option without the carryover or contamination problems often seen with purge and trap analysis. The HT3™ Automated Headspace Analyzer can run both static and dynamic headspace analysis within the same schedule and the system has the Method Optimization Mode (M.O.M.) which can automatically modify headspace parameters in order to determine optimum experimental conditions. The different soil matrices however did pose some compound recovery issues when using the headspace analyzer and matrix would have to be a consideration when doing this analysis. The Atomx P&T concentrator/Multimatrix Autosampler is an excellent system for determining VOCs in a soil matrix. This system has the distinct advantage of being able to run low level, in vial purge, P&T and also has an automated solvent extraction option for P&T. For low level VOC analysis, the in vial purge technique detected VOCs very well in clay, however both the sand and soil matrices affected compound recoveries. Solvent extraction on the other hand, proved to be the best choice in determining VOCs in difficult matrices as there were no issues with compound recovery no matter what matrix was being analyzed.