

Gas Chromatography

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Soil Gas Analysis: The Solution for Extending the Hydrocarbon Range of TO-17

Introduction

Soil gas (also known as soil vapor) refers to the air occupying the interstitial space between soil particles. Soil gas may contain

volatile and/or semi-volatile compounds which enter this space as they volatilize and migrate away from a contaminated sub-surface water and/or soil source.

Soil vapor becomes a bigger concern when these compounds find a pathway into a confined space situated on or near the source of contamination. Whether the building is residential or commercial, the impact to human health can be significant.

The sampling and analysis of soil gas poses several unique challenges when compared to indoor or ambient air monitoring. For instance, soil gas often has higher moisture content and possibly a broader range of compounds. Because of the confined space, typical sites can be very contaminated. Thus sorbent tubes and the analytical system need to deal with this while providing accurate data at the low detection limits required for the toxic regulated compounds.

PerkinElmer, with assistance from CARO Analytical Services, has designed a new thermal desorption tube that successfully accommodates the challenges of soil gas sampling and analysis while outperforming the regulatory criteria a detection limits, accuracy and analyte range.

EPA Method TO-17 is used to quantitatively analyze toxic volatile compounds in air samples after these compounds have been collected onto sorbent tubes.

Objectives

The objectives for designing this new sorbent tube were to select adsorbents with optimized weight ratios that would:

- Extend the analyte range past naphthalene (the limit of typical adsorbent tubes).
 - Many sites contain compounds in the diesel boiling point range. These compounds need to be recovered from the sorbents so the tube is clean for resampling and because there may be required target compounds.
 - Achieve excellent recovery for the higher boiling components during desorption.
- Ensure the most volatile compounds such as vinyl chloride are retained during sampling.
- Ensure the adsorbents selected did not produce target artifacts which may result in false positives.
- Enable “quick clean up” of the tubes so that the primary desorption process would lend them available for re-sampling, reducing analytical cost.
- Maintain water management inherent with using hydrophobic adsorbents.
- Increase sampling volumes to attain regulatory detection limits while enabling the recollection of the sample in case reinjection of the same sample is required.

Operation: The PerkinElmer TurboMatrix 650 Thermal Desorber (ATD):

After samples have been collected (or standards have been injected) onto the sorbent tubes, these tubes are loaded onto the ATD autosampler. The instrument inserts the tube into the primary desorption path. A leak check is performed on both the sample tube and the concentrator trap to ensure sample integrity. Additionally, an impedance check may be performed on the tube and/or the trap to validate that the packing has not changed with time and use (Figure 1).

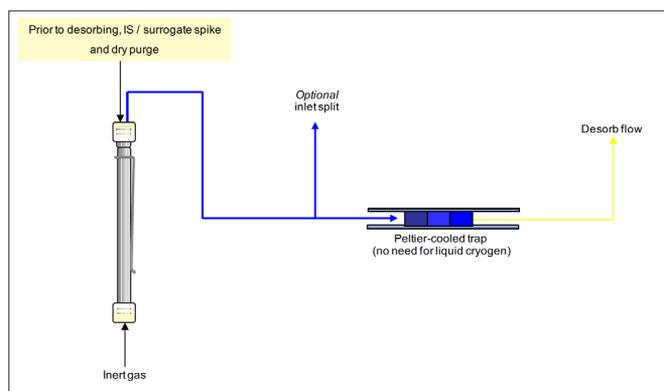


Figure 1. Sample tube desorption.

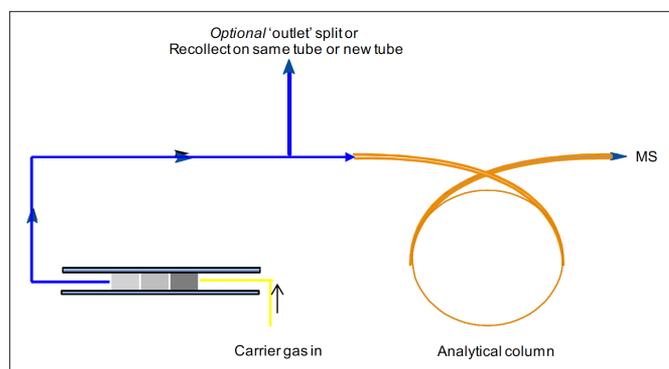


Figure 2. Trap desorption.

After these steps are performed, an inert gas flows through the tube, automatically introducing a gaseous internal standard onto the tube (this step is optional) while performing a dry purge to rid the tube of oxygen and water. Following the dry purge, a heater is placed onto the tube. Using a combination of heat, flow and time, the contents of the tube are transferred to the concentrator (cold) trap (Figure 1).

The concentrator trap employs a Peltier (electronic) cooler instead of liquid cryogen to achieve the trap's lower temperature (as low as $-35\text{ }^{\circ}\text{C}$); however for this application, the cold trap during primary desorb is at $10\text{ }^{\circ}\text{C}$. The low dead volume trap contains hydrophobic sorbents; therefore, the analytes are focused on the focusing trap using sorbents and low temperature so breakthrough of this analyte set does not occur.

After the contents of the tube are adsorbed onto the concentrator trap, the trap is heated rapidly, and the contents of the trap are introduced into the GC analytical column in a narrow band (Figure 2).

The system offers additional flexibility. For highly concentrated samples, two splitters may be employed: an inlet split between the sample tube and the concentrator trap, and an outlet split between the concentrator trap and the analytical column, enabling split ratios of several orders of magnitude. The inlet split may be disabled, and the outlet split may be used to recollect the sample onto the same tube or onto a different tube, preserving the sample for another injection (such as a sample dilution). For trace-level samples, splitless injection may be performed.

A surrogate can be automatically spiked onto all tubes prior to sampling incorporating additional validation of sample.

Experiment

The instruments used in this application were the PerkinElmer TurboMatrix™ Thermal Desorber 650 (ATD), Clarus® 690 Gas Chromatograph (GC) and the Clarus SQ 8 Mass Spectrometer.

A high temperature volatile column was used, enabling extension of the hydrocarbon range past naphthalene while still focusing the most volatile compounds.

The mass spectrometer was operated in full SCAN mode, achieving the necessary detection limit criterion without the need for selective ion monitoring (SIM).

86 target compounds and diesel were investigated. The following standards were purchased from Restek® Corporation:

- 502.2 calibration mix #1 (Restek Catalog #30042) containing six gases.
- Single component 1,3-butadiene (Restek Catalog # 30622)
- 8260B Mega Mix (Restek Catalog #30633) containing 76 VOCs
- 1-methylnaphthalene, anthracene, fluorene and phenanthrene from separate ampules
- Diesel purchased from a nearby petro station

The standards were diluted with purge and trap grade methanol to attain the required concentrations for the experiments.

Breakthrough and Recovery studies were performed by spiking the thermal desorption tubes with a high concentration of the following analytes (to mimic a contaminated site):

- 300 ng of 502.2 calibration mix #1 (six gases)
- 300 ng of 1,3-butadiene
- 300 ng of 8260B Mega Mix
- 200 ng of the four polynuclear aromatic hydrocarbons (PAHs)
- 10 µg of diesel

After spiking three tubes, each tube was connected to a clean tube referred to as the breakthrough check tube. Each set (spiked tube connected to breakthrough check tube) was placed on a manifold that accommodated three sets. 100 mL/min of humidified nitrogen (82%) was simultaneously passed through the tubes for 100 minutes at 100 mL/min to simulate a 10 liter sampling volume. Figure 3 provides an illustration of the experiment.

The goal was that all target compounds would not be detectable in the breakthrough check tube (the second tube in the series). Recovery (completeness) of the desorption process was confirmed by re-analyzing the spiked tube. A trap test was first analyzed to confirm complete desorption from the cold trap, and then an empty (blank) tube was analyzed prior to the re-analysis of the spiked tube to confirm instrument cleanliness.

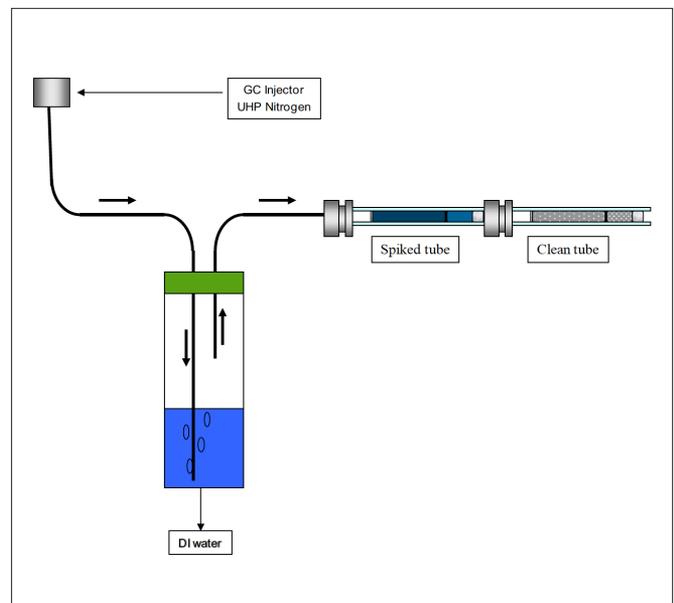


Figure 3. Illustration of breakthrough experiment.

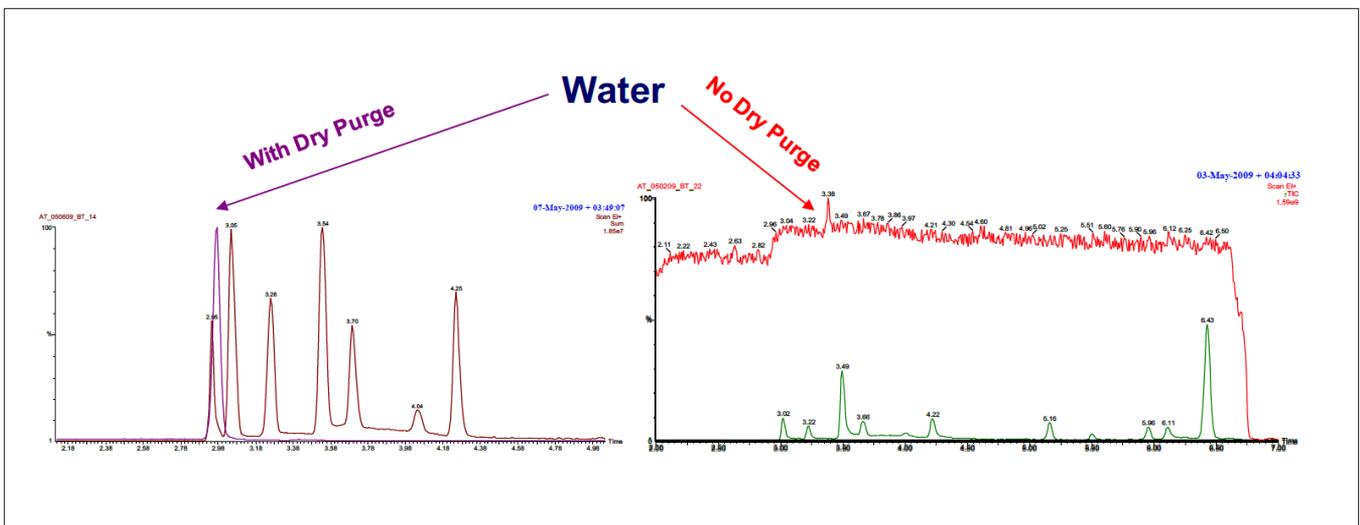


Figure 4. Dry Purge efficiently drives off moisture.

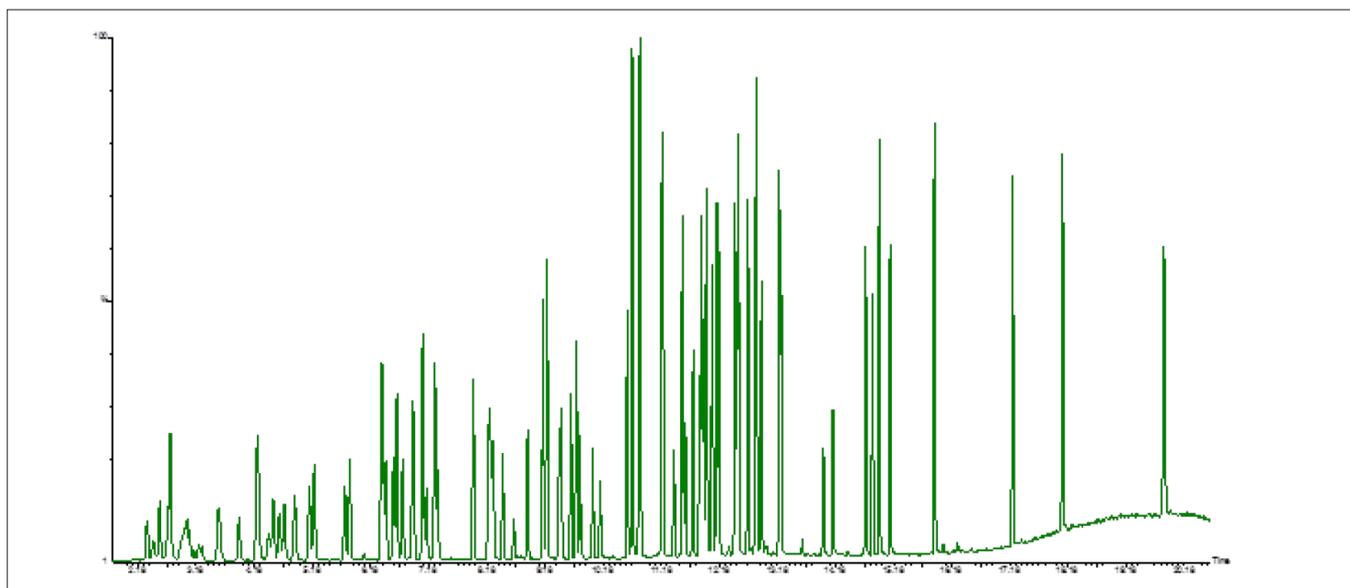


Figure 5. Example chromatogram at 0.5 ng on column.

Water Management (i.e. minimized retention of water) was determined by starting the MS scan at 15 AMU instead of 35; therefore, enabling the mass characteristic of water (18) to be acquired. Figure 4 illustrates the level of water management achieved by these tubes and system, essentially reducing water to instrument background water levels comparing a dry purged tube to a tube that was not dry purged.

Instrument Precision was investigated by spiking 10 tubes with a 20 ng VOC standard (0.5 ng on column). Figure 5 represents a total ion chromatogram (TIC) of the 20 ng standard used for precision.

Dynamic Range was evaluated over four orders of magnitude, from 0.05 ng to 250 ng spiked onto the tube for a 1 liter sample volume. Therefore, 0.05 ug/m³ would be the reporting limit for a 1 liter sample volume.

Minimum Detection Limits were also investigated.

Results

With 10 liters of humidified nitrogen flowing through the tubes, the breakthrough was minimal, observed only on one of the most volatile compounds, dichlorodifluoromethane (Freon-12) at 1% as documented in Table 1. The EPA allows 5% so this target meets EPA criterion.

One of the most toxic volatile gases, vinyl chloride, exhibited no detectable breakthrough, despite the fact that the concentration and humidity of the tubes were very high. Since the toxicology on vinyl chloride is well documented, retaining this compound is critical.

All compounds achieved over 99.9% recovery except for a few of the PAHs that achieved better than 98% recovery as documented in Table 2. Pyrene can be recovered from the adsorbent using a temperature of 325 at 90% recovery. If the temperature is increased to 360, pyrene recovered at 99%.

As demonstrated in Table 3, the data collected on precision, linearity and reporting limits is excellent for all classes of compounds and out performs all regulatory requirements. The reporting limits are calculated using a 1 liter sample volume. The dynamic range achieved was four orders of magnitude across the target component list.

Thermal desorption is a very cost effective, accurate technique for the sampling and analysis of air samples.

- Sorbent tubes are small and light, making them easy to transport, thus reducing shipping costs compared to other techniques.
- Sorbent tubes are cleaned during the desorption process, rendering them available for immediate re-sampling. The tube can be verified as being clean with a short GC/MS analysis.

Water management is rigorous and automatic. Eliminating or reducing water entering the analytical system prevents the “quenching” of the response of target analytes, yielding accurate data and enhanced detection limits.

Sample integrity is preserved using the PerkinElmer TurboMatrix Thermal Desorber. The following automated processes ensure sample integrity:

- A surrogate may be automatically spiked onto the tube prior to sending the tube into the field for sampling.
- The sample tube and the concentrator trap is leak checked prior to desorption.
- If desired or required, an internal standard is automatically spiked onto the tube.
- A tube impedance check is performed on the tube to ensure packing is consistent (optional).
- The sample may be recollected onto a new tube or the same tube if there is a need to re-analyze, or if the sample needs to be preserved for legal purposes.

Table 1. Results of gases from breakthrough (BT) experiment.

Compound	%BT
Dichlorodifluoromethane	1.0
Chloromethane	nd
Vinyl Chloride	nd
1,3-Butadiene	nd
Bromomethane	nd
Chloroethane	nd
Trichlorofluoromethane	nd
nd is non-deducted	

Table 2. Results of recovery for heavier compounds .

Component	% Recovery
1-Methylnaphthalene	99.7
Anthracene	99.8
Florene	99.4
Phenanthrene	98.8
Diesel	99.9

The SVI sorbent tubes enable excellent recoveries of a broad range of hydrocarbons (C₃ through C₂₆), from the most volatile Freons through to the diesel range hydrocarbons. Polar components are easily released during the desorption process, enabling quantification as well.

Table 3. Analytical performance results.

Class of Compound	# of Analytes Per Group	Linearity (0.05 to 250 µg/m ³)*		Precision	Reporting Limit 0.05 µg/m ³
		r ²	Ave RF (% RSD)	(n=10)	S/N at 0.05 µg/m ³
Gases	7	0.9994	9.07	7.39	530:1
Aliphatic Hydrocarbons (halogenated)	35	0.9996	14.00	4.80	560:1
Aromatics (halogenated)	9	0.9997	13.30	2.58	1350:1
Aromatics (non-halogenated)	14	0.9996	10.27	1.91	1220:1
Polynuclear Aromatic Hydrocarbons (PAHs)	5	0.9997	8.69	3.56	570:1
Others	13	0.9996	9.26	3.19	560:1

Conclusion

In conclusion, using the PerkinElmer SVI thermal desorption tubes in conjunction with EPA TO-17, to collect and analyze soil gas, is the most cost effective, accurate, and precise technique available today.