APPLICATION NOTE

Gas Chromatography/
Mass Spectrometry

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Analysis of Volatile Organic Compounds (VOCs) in Air Using US EPA Method TO-17

Introduction

Optimized methods are needed for the analysis of toxic compounds in air to understand the impact to human health. People breathe approximately 20,000 liters of air a day so this concern is significant.

EPA Method TO-17[1] is used to determine toxic compounds in air after they have been collected onto sorbent tubes. These tubes can either adsorb specific compounds or adsorb a broad range of compounds, quantitatively.

Adsorbent tubes have many applications in the investigation of volatile organic compounds (VOCs) found in EPA Method TO-17. Examples include indoor air, fence line, stack, workplace, personal monitoring and soil gas. The type of tube used, and whether the sampling is passive or active, depends upon the need at the particular site being investigated.

This application note demonstrates that the PerkinElmer TurboMatrix™ Thermal Desorber and the PerkinElmer Clarus® SQ 8 GC/MS will meet and exceed the criteria set forth in EPA method TO-17. Detailed instrument method parameters are presented, with precision, recovery, linearity and detection limit results.

Experiment

The instruments used in this application were the PerkinElmer TurboMatrix Automated Thermal Desorber 650 (ATD), the Clarus 680 Gas Chromatograph (GC), the Clarus SQ 8 Mass Spectrometer (MS), detailed analytical parameters are described in Table 1.

A PerkinElmer Elite 624 sil column (60 m x 0.25 mm x 1.4 µm) was used. This new column has an advantage of enabling higher oven temperatures than traditional 624 phase columns. The 624 column was chosen because it focuses and separates the volatiles efficiently, in addition to having an adequate temperature range. Also, it is a common column currently in use for most volatile methods.

The enhanced sensitivity of this analytical system enabled the mass spectrometer acquisition to be performed in full scan mode opposed to Single Ion Monitoring (SIM) mode. This enables the positivity identification via library matching to be performed.

Eighty-two compounds were investigated. The standards were purchased from Restek Corporation, as follows:

- 502.2 calibration mix #1 (Restek Catalog #30042) that contains the six gases.
- 1,3-butadiene (Restek Catalog #30622).
- 8260B Mega Mix (Restek Catalog #30633) that contains 76 VOCs.

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

After samples (or standards) have been introduced onto the sorbent tubes, these tubes are placed onto the ATD autosampler. The instrument inserts the tube into the primary desorption path. Prior to injection, a leak check is performed on both the sample tube and the concentrator trap to ensure sample integrity. An impedance check may be performed on the tube and/or trap at this time to validate that the tube and trap packing has not changed. After the leak check and optional impedance test (s) are performed, a gaseous internal standard can be spiked onto the ATD tube using an inert gas flow.

Table 1. Analytical parameters.

Thermal Desorber Parameters		GC Parameters		MS Parameters	
Tube Desorb Temp	325 °C	Initial Oven Temp	35 °C	Mass Range (amu)	35 to 300
Tube Desorb Time	7 min	Oven Hold 1	4 min	Filament Delay	none
TubeDesorb Flow	45 mL/min	Ramp 1	5 °C/min	Start Time	0.0 min
Concentrator Trap Low	10 °C	2nd Oven Temp	110 °C	End Time	29.5 min
Concentrator Trap High	325 °C	Oven Hold 2	0.0 min	Scan Time	0.35 min
Concentrator Trap Hold	5 min	Ramp 2	12 °C/min	Interscan Delay	0.04 min
Dry Purge Time	2 min*	3rd Oven Temp	195 °C		
Dry Purge Flow	50 mL/min	Oven Hold 3	0.0 min		
Dry Purge Temperature	ambient	Ramp 3	20 °C/min		
Column Flow	1.8 mL/min	Final Oven Temp	250 °C		
Inlet split	10 mL/min	Oven Hold 4	1.0 min		
Recollect (or outlet split)	18 mL/min				
Column Flow During Trap D time	1.8 mL/min	Column: PE Elite— 624-60 m x 0.25 mm x 1.4 µ			
GC Cycle Time (Clarus 600 GC)	29.8 min				

**time depends upon humidity at time of sampling*

A dry purge of the tube is used to rid the tube of oxygen and water. A heated dry purge may be performed, if required.

Following the dry purge, desorption is initiated using a combination of heat, flow and time to transfer the tube's contents to the electronically cooled concentrator trap or cold trap. This process is graphically demonstrated in Figure 1.

The cold trap uses a Peltier (electronic) cooler instead of liquid cryogen to meet the cold trap's lower temperature (as low as minus 35 °C). This low dead volume cold trap (Figure 2) contains a hydrophobic adsorbent (s) allowing any residual moisture to break through while retaining the target compounds.

After the contents of the sample tube are concentrated onto the cold trap, the cold trap is heated rapidly thus releasing the analytes onto the analytical column in a narrow band (Figure 3).

The system offers additional flexibility. For concentrated samples, two splitters may be employed: an inlet split between the sample tube and the cold trap, and an outlet split between the cold trap and the analytical column, enabling high split ratios if required. 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. For trace level samples, splitless injection may be performed.

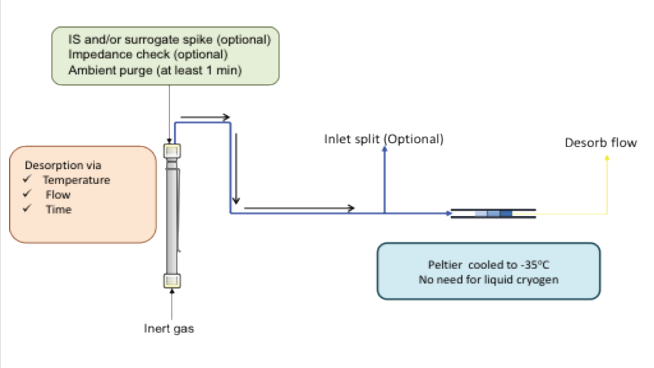

Figure 1. Sample tube desorption.

Instrument precision was investigated by spiking 10 tubes with a 20 ug/m^3 standard or 1.5 ng injected on column. Figure 4 represents a total ion chromatogram (TIC) of a standard injecting 3.25 ng on column. Dynamic range was evaluated from 0.05 to 250 ug/m^3 for a 1 L sample. The precision of the automated internal standard was investigated making 15 injections of the four internal standards.

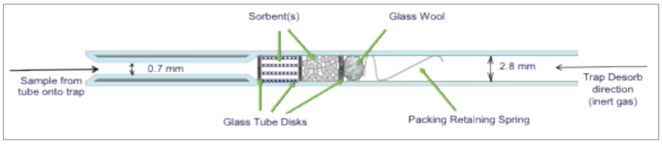

Figure 2. Concentrator (cold) trap.

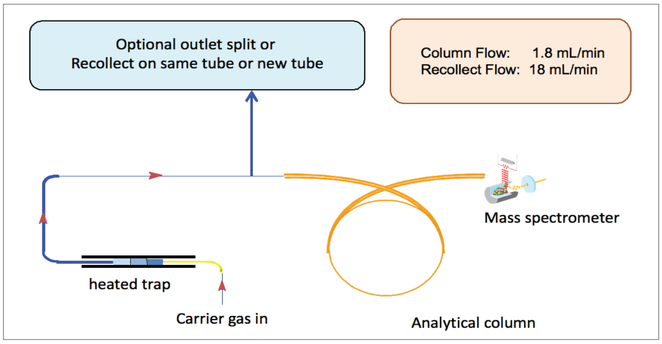

Figure 3. Trap desorption (analytes are desorbed from the trap in the opposite direction from which they were adsorbed).

Results

Table 2 summarizes the results for precision, method dynamic range, and signal to noise at the reporting limit. The compounds are grouped into classes, and the average of each class is reported.

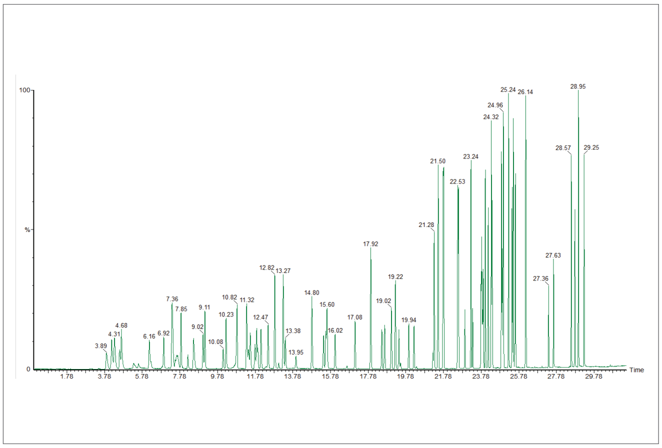

Figure 4. 3.25 ng on column total ion chromatogram.

The precision, linearity, and reporting limit data is excellent for all classes of compounds and exceeds method criteria even for regions regulating the most challenging reporting limits. Reporting limits are calculated using a 1 liter sample volume. Even though TO-17 suggests a maximum sampling volume of 4 liters, the sampling volume was safely extended to 10 liters enabling enhanced detection limits satisfying several regulatory regions who require a 10 L volume. A dynamic range of four orders of magnitude across the component list was achieved. The curves and %RSD presented in Table 2 were processed using external standard to demonstrate that even IS uncorrected data was compliant. Table 4 demonstrates repeatability of the IS using the automated internal standard accessory.

Figure 5 represents examples of integrated quantitation ions for six important target compounds at 0.05 ng spiked on tube or 0.05 ug/m^3 for a 1 L sample volume.

Table 2. Results for linearity, precision and signal to noise (s/n) at the reporting limit.

Class of Compound	# of Analytes Per Group	Linearity (0.05 to 250 µg/m^3)*		Precision	Reporting Limit
		r^2	Ave RF	(n=10)	S/N at 0.05 µg/m^3)
Gases	7	0.9994	9.07	7.39	530:1
Non-aromatic Halogens	35	0.9996	14.00	4.80	560:1
Halogenated Aromatics	10	0.9997	13.30	2.58	1350:1
Aromatics (Non-halogenated)	17	0.9996	10.27	1.91	1220:1
Others	13	0.9996	9.26	3.19	560:1

**The dimensions are in ug/m^3. If reporting in ppbv, the reporting limits will be lower. For example, 0.05 ug/m^3 toluene is equal to 0.01 ppbV*

Table 3. Relative Standard Deviation (%RSD) results using the TMX Thermal Desorber Automated Internal Standard Addition from 15 consecutive injections (n=15).

Internal Std	Fluorobenzene	1,4 Difluorobenzene	Chlorobenzene-d_5	BFB
RT	15.10 min	15.27 min	21.37 min	23.27 min
Quant ion	96	114	117	95
%RSD	1.34	1.29	0.53	0.98

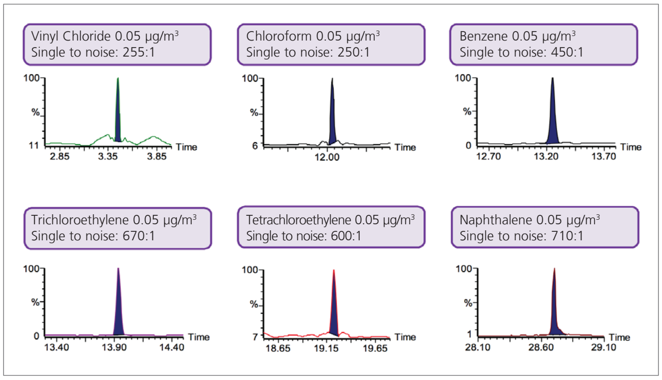

Figure 5. Graphical representation of six (6) important targets based on 1 liter sample volume.

Conclusion/Summary

- Thermal desorption is a very cost effective technique in the sampling and analysis of VOCs in air.
  - Sorbent tubes are small and easy to transport reducing shipping costs when compared to other techniques.
  - Sorbent tubes occupy significantly less laboratory real estate than other air media.
  - Sorbent tubes are cleaned during the desorption process rendering them available for immediate re-sampling, therefore enhancing efficiency and productivity.
- The analytical results exceed method criteria; in particular, detection limits are exceeded for all regulatory agencies with a 1 L sample volume acquired in full scan.
- Water management is rigorous and automated. Eliminating or reducing water entering the analytical system prevents the "quenching" of the response of the target analytes providing accurate data and enhanced detection limits.
- Sample integrity is preserved using the PerkinElmer TurboMatrix Thermal Desorber. The following processes are automated:
  - A surrogate may be spiked onto the tube prior to sending the tube into the field for sampling.
  - The sample tube and the cold trap is leak checked prior to sampling ensuring the intended target amount from the tube and the trap on column is not affected by leaks of tube and cold trap which would affect quantitative accuracy.
  - An internal standard may be spiked onto the tube prior to analysis (optional). Internal standard calibration compensates for any variation in sample volume introduction enhancing accuracy. In addition, if there are no targets detected in the sample tube; however, the internal standard is recovered, this validates the tube was desorbed and that an injection was made from the tube.
  - A tube impedance check may be performed on the tube to ensure packing for each tube is consistent (optional).
  - The sample may be recollected onto a new tube or the same tube if there is a need to re-sample or if the sample needs to be preserved for legal purposes.
- Sorbent tubes enable excellent recoveries for a broad boiling point component. The range for the patented SVI tube is from the most volatile Freons™ through to diesel range hydrocarbons (C3 to C26). In addition, thermal desorption is ideal for the recovery of polar components.

Using the U.S. EPA method TO-17 with sorbent tubes for air sampling is a very cost effective, accurate and precise technique. Sorbent tubes offer the broadest component range, and offer superior detection limits over other techniques.

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1. Compendium Method TO-17, Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes.

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