

Thermal Desorption Technical Support

Note 86a: US EPA Method TO-17 for Monitoring Air Toxics in Ambient Air Using Sorbent Tubes and Automated, Cryogen-free Thermal Desorption

Application Note

Environmental, Tube, TO-17, Air Monitoring

MARKES
international

Introduction

Volatile (vapor-phase) organic air toxics or Hazardous Air Pollutants (HAPs) are monitored in many industrial and urban environments as a measure of air quality. They range in volatility from methyl chloride to hexachlorobutadiene and trichlorobenzenes, and include polar as well as nonpolar compounds. Several national and international standard methods have been developed for air toxics and related applications including US EPA Method TO-17 (Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes).

In response to increasing demand for ambient air toxics measurement, cryogen-free thermal desorber (TD) technologies have been developed, presenting an automated, method-compliant analytical platform for both tubes and canisters (for US EPA Method TO-15, see TDS 81). The latest systems typically feature innovations such as repeat analysis for tubes, together with internal standard addition options for both canister and tube operation.

Description of the TD-GC/MS Analytical System

The analytical system used for this study comprised a Markes International Series 2 ULTRA-UNITY TD (Figure 1) coupled to a GC/MS.

Using this TO-17 compliant system, the sorbent tubes were heated in a flow of carrier gas transferring the analytes to an electrically cooled, sorbent-packed focusing trap inside the UNITY 2.

Extensive evaluation work was carried out to determine the best combination of sorbents and trapping temperatures for the focusing trap. A combination of Tenax, Carboxen 1003 sorbents held at a trapping temperature of 25 °C, was ultimately found to work best, offering both quantitative recovery of target compounds and selective elimination of water.



Figure 1. ULTRA-UNITY 2.



Agilent Technologies

N.B. Quantitative recovery of compounds as volatile as propylene from purge volumes up to 2 L has also been demonstrated using this trap under these focusing conditions.

Once the process of transferring vapors from the sample/sorbent tube to the focusing trap was complete (primary desorption), the trap was purged with dry carrier gas in the sampling direction to remove residual water. Then, the flow of carrier gas was reversed, and the trap heated rapidly. The retained organics were desorbed into the carrier gas stream and transferred/injected into the GC analytical column.

Desorption of a UNITY 2 focusing trap is so efficient, that splitless analysis is possible without significant peak broadening; that is, all of the retained organics can be transferred to the analytical column in a narrow band of vapor, ensuring optimum sensitivity.

Air sampling tubes

Air Toxic Analyzer (ATA) tubes, packed with a combination of Carbograph 1TD and Carboxen 1003, were used for most of this study. This sorbent combination has demonstrated quantitative retention of air toxics, including the most volatile target compounds, from over 2 L* of air at 25 °C. Pumped air sampling flow rates were maintained at 50 mL/min.

Universal tubes packed with Tenax TA, Carbograph 1TD, and Carboxen 1003 were used for some experiments. Universal tubes limit retention volumes to 1 L for the most volatile air toxics, but facilitate analysis of labile monoterpenes such as D-limonene.

***Note:** Breakthrough volumes can be compromised by high humidity or elevated ambient temperatures.

Analytical Conditions

This project was carried out using an Agilent J&W DB-624 column and a mixed air toxic standard containing over 60 analytes, ranging in polarity and volatility.

Sample preparation

A 62 component 1 ppm gas standard in nitrogen, available from Markes International (p/n CGS15-1PPM), in combination with an air actuated 6-port Valco valve was used to inject 1 mL aliquots of standard gas, carried in pure nitrogen, into the sorbent tubes (Figure 2).

Parameter	Value
UNITY 2 parameters	
Cold trap:	Markes Air Toxic Analyser/Soil Gas trap (p/n U-T15ATA-2S)
Tubes:	Markes Air Toxic Analyser tubes (p/n C2-AXXX-5270) Markes Universal stainless steel tubes (p/n C3-AXXX-5266) packed with a combination of Tenax, Carbograph 1TD and Carboxen 1003
Cold trap low temperature:	25 °C
Tube desorption temperature:	320 °C
Tube desorption time:	10 minutes
Trap purge time:	2.0 minutes
Cold trap high temperature:	320 °C for 3 minutes
Split ratio:	splitless or 10:1 outlet split
Trap heating rate:	40 °C/s
TD flow path:	140 °C
GC parameters	
Carrier gas:	He
Column:	Agilent DB-624, 60 m × 0.32 mm, 1.80 µm
Constant pressure mode:	10 psi
Temperature program:	35 °C (5 minutes), 5 °C/min to 230 °C (0 minutes)

MS conditions	
MS source temperature:	230 °C
MS quadrupole temperature:	150 °C
MSD transfer line temperature:	200 °C
Full scan mode mass range:	35-300 amu

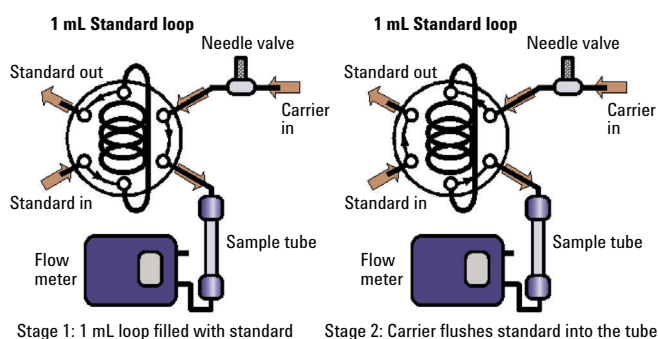


Figure 2. Apparatus for loading 1 mL aliquots of standard gas onto sorbent tubes in a stream of pure nitrogen.

Results and Discussion

Figure 3A shows the chromatogram obtained for a sample equivalent to 1 L of 1 ppb standard analyzed splitless.

Figure 3B shows the chromatogram obtained for a sample

equivalent to 1 L of 1 ppb standard analyzed with a 10:1 outlet split. The peak at 4.5 minutes was due to SO_2 released from the carbon molecular sieve sorbent used at the back of the sampling tubes.

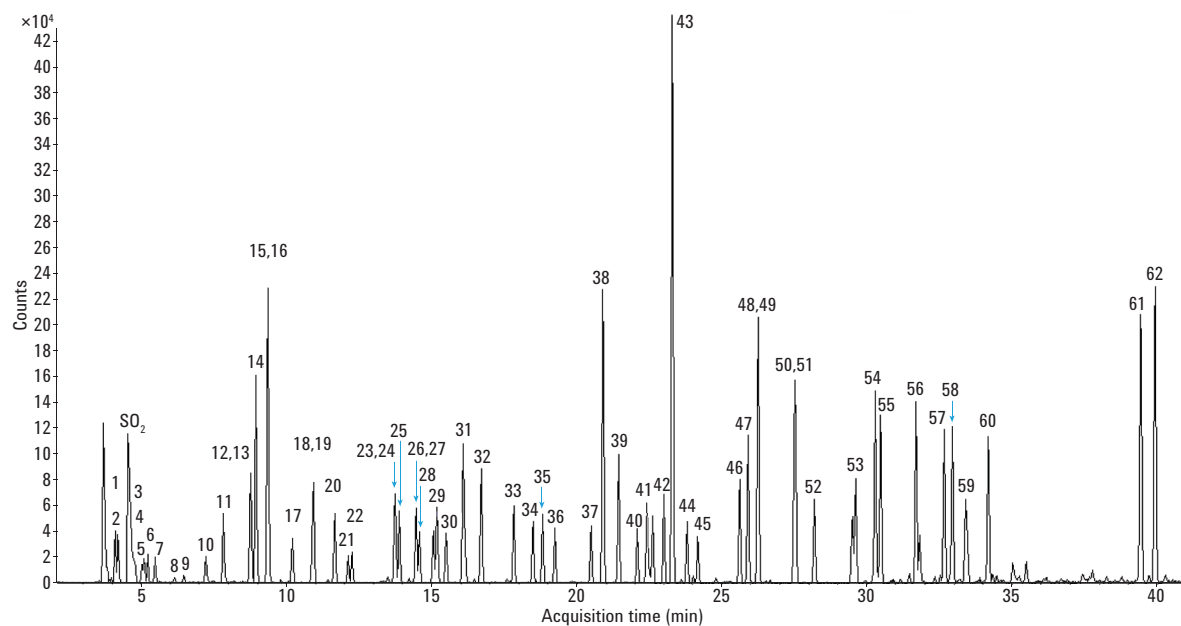


Figure 3A. Sample equivalent to 1 L of a 1 ppb standard analyzed splitless using ATA tubes and an Agilent J&W DB-624 column.

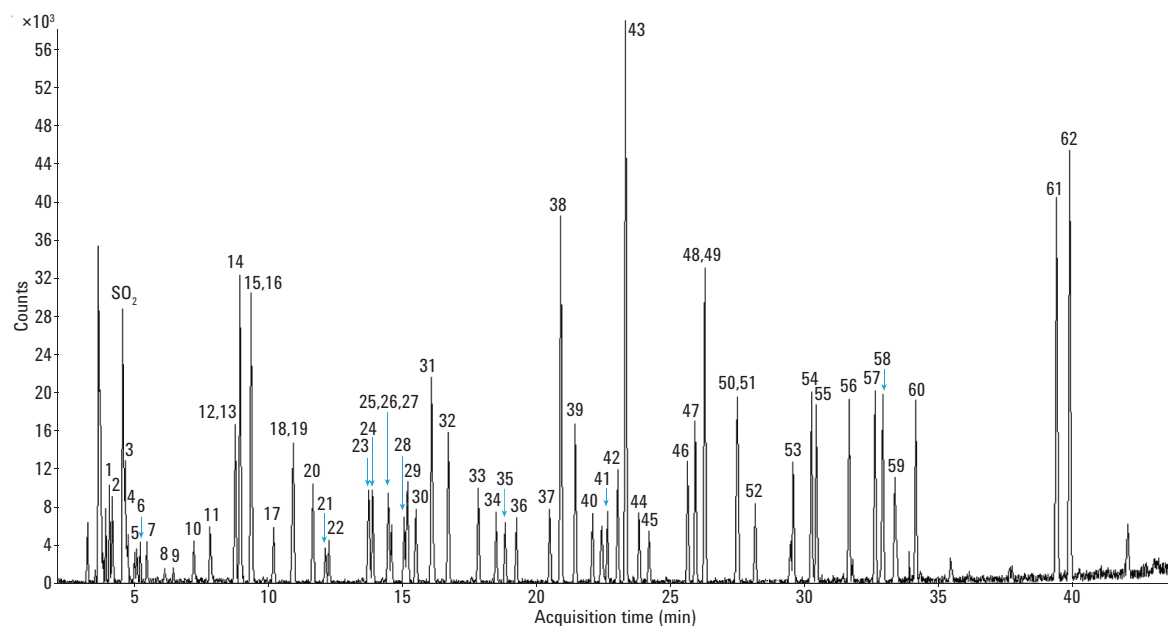


Figure 3B. Sample equivalent to 1 L of a 1 ppb standard analyzed with a 10:1 split using ATA tubes and an Agilent J&W DB-624 column.

Table 1. Elution order for the air toxics standard run on an Agilent J&W DB-624 column.

No.	Compound	No.	Compound	No.	Compound
1.	Propylene	21.	1,1-Dichloroethane	41.	1,1,2-Trichloroethane
2.	Dichlorodifluoromethane	22.	Vinyl acetate	42.	Tetrachloroethylene
3.	1,2-Dichlorotetrafluoroethane	23.	<i>trans</i> -1,2-Dichloroethylene	43.	Methyl <i>n</i> -butyl ketone
4.	Methyl chloride	24.	Methyl ethyl ketone	44.	Dibromochloromethane
5.	Chloroethane	25.	Ethyl acetate	45.	1,2-Dibromoethane
6.	1,3-Butadiene	26.	Tetrahydrofuran	46.	Chlorobenzene
7.	Vinyl chloride	27.	Chloroform	47-50)	<i>o</i> -, <i>m</i> -, <i>p</i> -Xylene + ethylbenzene
8.	Methyl bromide (bromomethane)	28.	1,1,1-Trichloroethane	51.	Styrene
9.	1,2-Dichloroethane	29.	Cyclohexane	52.	Tribromomethane
10.	Trichlorotrifluoroethane (Freon 113)	30.	Carbon tetrachloride	53.	1,1,2,2-Tetrachloroethane
11.	Ethanol	31.	Benzene	54.	Trimethylbenzene
12.	1,1-Dichloroethylene	32.	<i>n</i> -Heptane	55.	Trimethylbenzene
13.	1,1,2-Trichlorotrifluoroethane	33.	Trichloroethylene	56.	1-Ethyl-4-methyl benzene
14.	Acetone	34.	1,2-Dichloropropane	57.	Dichlorobenzene
15.	Carbon disulfide	35.	1,4-Dioxane	58.	Dichlorobenzene
16.	Isopropyl alcohol	36.	Bromodichloromethane	59.	Chloromethylbenzene (<i>alpha</i>)
17.	Methylene chloride	37.	<i>cis</i> -1,3-Dichloropropene	60.	Dichlorobenzene
18.	<i>tert</i> -Butyl methyl ether	38.	Methyl isobutyl ketone	61.	1,2,4-Trichlorobenzene
19.	<i>cis</i> -1,2-Dichloroethylene	39.	Toluene	62.	Hexachloro-1,3-butadiene
20.	<i>n</i> -Hexane	40.	<i>trans</i> -1,3-Dichloropropene		

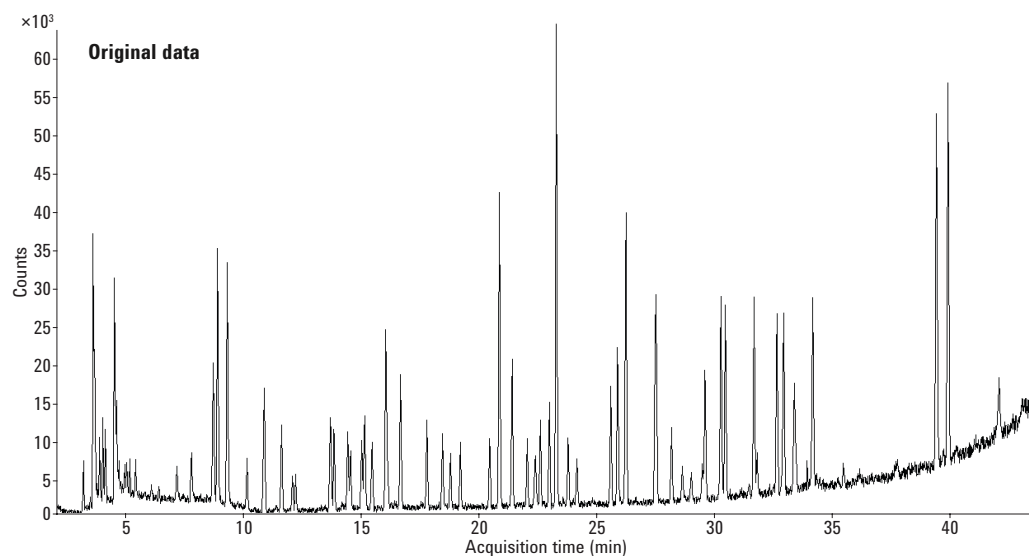


Figure 4. 1 L of a 1 ppb air toxics standard, as shown in Figure 3B. Note the minor baseline anomaly due to residual water early in the run and increasing column bleed and noise as the GC oven reaches its top temperature.

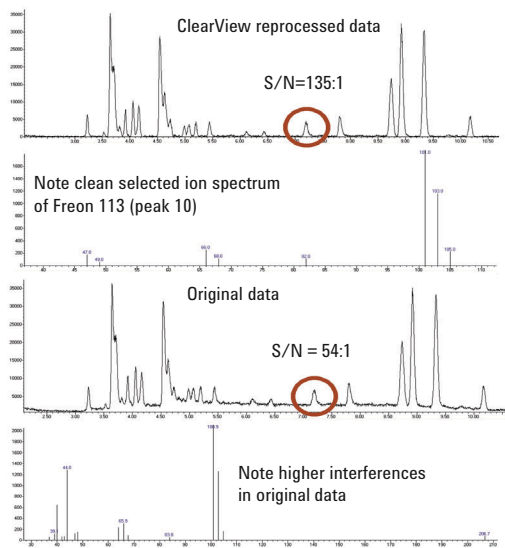


Figure 5. Expanded portions of the air toxics standard analyzed split (Figures 3B and 4).

Trap desorption efficiency leads to good peak shape and optimum sensitivity. Trap performance in this case is best illustrated by a close-up of the results for the challenging polar compound isopropyl alcohol (IPA) (Figure 6).

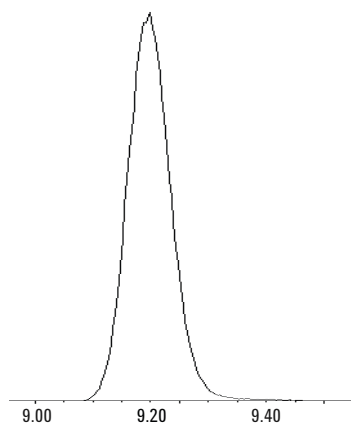


Figure 6. Peak shape for IPA at 1 ppb analyzed splitless using ATA tubes and extracted mass ion 45.

Minimum detection limits were found to be below 0.1 ppb for all 62 components tested under both 10:1 split and splitless conditions, assuming a minimum 1 L air/gas sample volume and full scan mode. Measurement at lower concentrations could readily be achieved using the MS in Selected Ion monitoring (SIM) mode.

Linearity

Figure 7 illustrates system linearity under splitless conditions with R^2 values of 0.99 for trichlorotrifluoroethane (Freon 113), dichlorodifluoromethane, chloroform, bromodichloromethane, and hexachloro-1,3-butadiene.

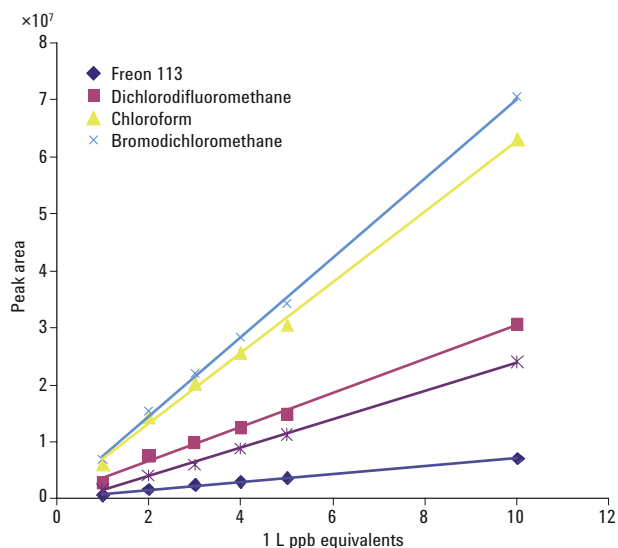


Figure 7. Linearity plots from 1 to 10 ppb standards collected using ATA tubes, and analyzed splitless.

Carryover for 1 L of 10 ppb standard analyzed splitless was less than 0.5% (Figure 8).

SecureTD-Q

Quantitative recollection of split flow facilitates repeat analysis and validation of TO-17 method/data. The repeat analysis of a sample equivalent to 1 L of 1 ppb air toxics standard, split 10:1 (Figure 9), demonstrates quantitative recovery across the analyte volatility range.

Six repeat analyses were carried out on samples equivalent to a 1 L volume of 1 ppb standard under splitless conditions. Table 2 shows example % relative standard deviation (RSD) for eight compounds, covering the volatility and polarity range of the standard. Typical RSDs were less than 6%.

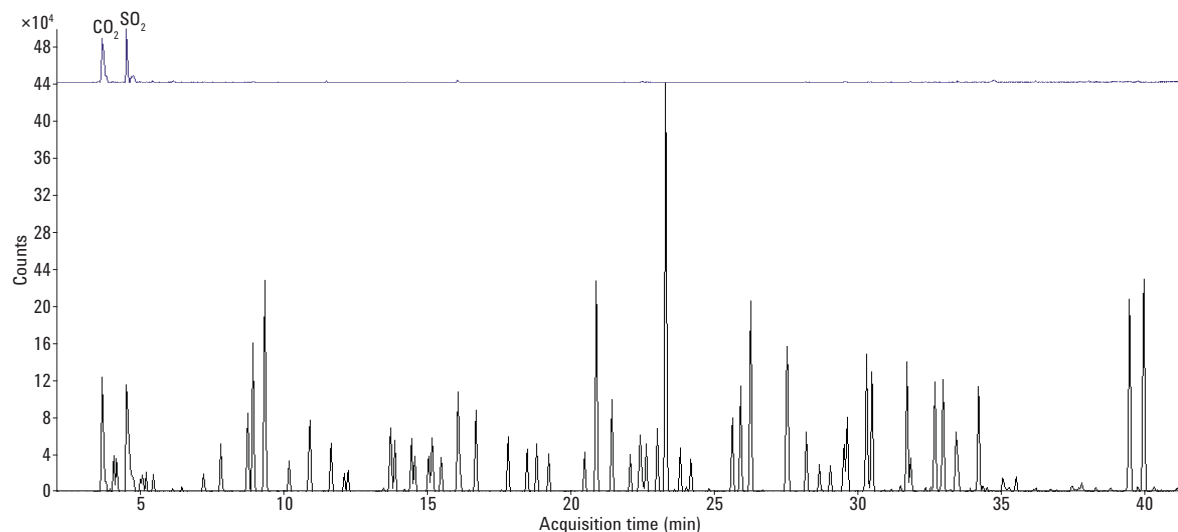


Figure 8. Carryover (blue) <0.5% from 1 L 1 ppb standard (black) analyzed splitless using ATA tubes.

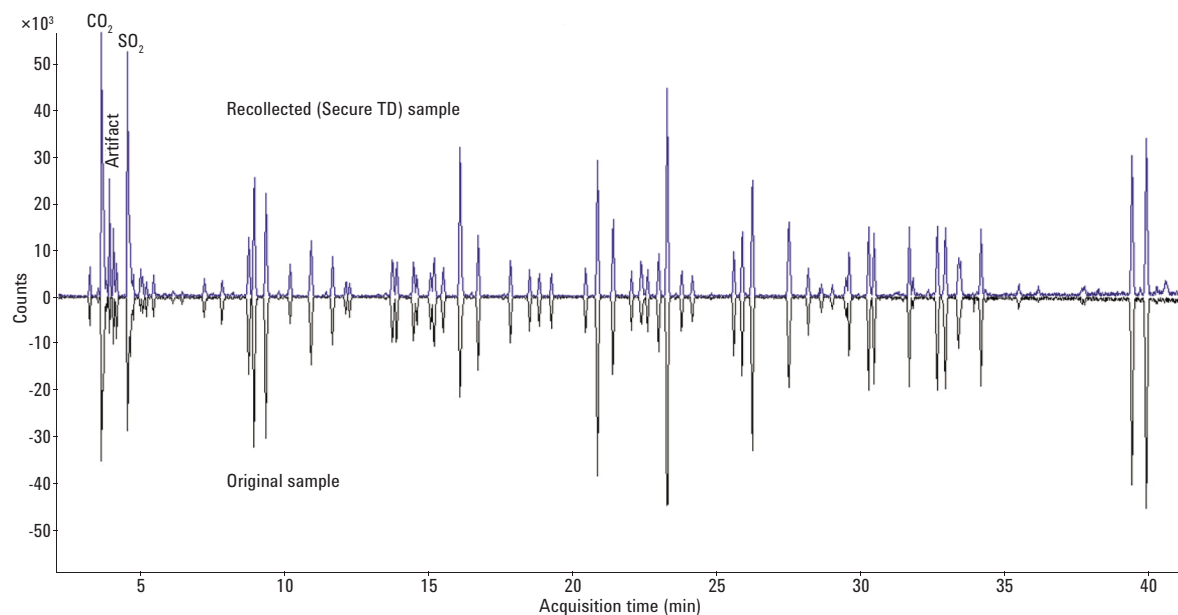


Figure 9. Recollection and repeat analysis results from a 1 ppb standard analyzed using ATA tubes and a 10:1 outlet split.

Table 2. System reproducibility demonstrated using eight compounds, covering a typical range of air toxic volatilities and polarities (n = 6). Conditions: ATA tubes, splitless.

Compound	% RSD
Dichlorodifluoromethane	2.8
1,3-Butadiene	5.5
Methylene chloride	3.4
Freon 113	1.8
Chloroform	1.8
Benzene	6.0
Toluene	1.7
Hexachloro-1,3-butadiene	3.8

Real air samples

Real air samples were collected onto Universal sorbent tubes. A FLEC pump was used to sample at a flow rate of 50 mL/min for 20 minutes giving a total volume of 1 L in each case. Three different ambient locations were sampled: office, laboratory, and semirural outside air. Each sample tube was analyzed splitless using a full scan MS method from 10-300 amu. The data were processed using ClearView and overlaid (Figure 10).

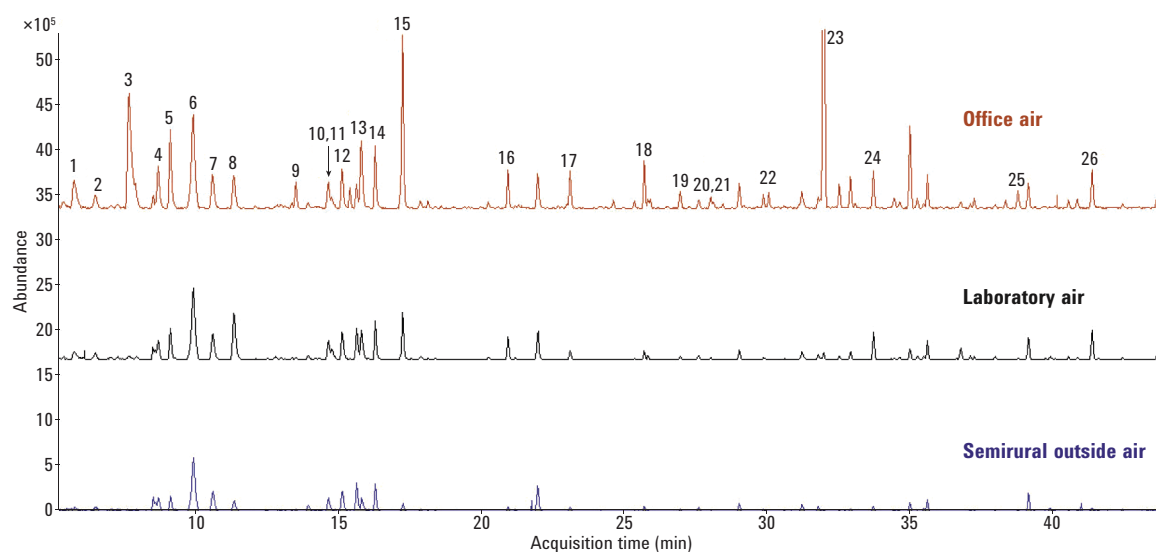


Figure 10. Chromatograms from three 1 L real air samples collected using Universal sorbent tubes and desorbed splitless.

Table 3. Selected compounds detected from three real air samples, run splitless.

No.	Compound	No.	Compound
1.	Methanol	14.	Acetic acid
2.	2-Methyl butane	15.	1-Methy-2-propanol
3.	Ethanol	16.	Toluene
4.	Acetone	17.	Hexanal
5.	Isopropyl alcohol	18.	Xylene
6.	2-Methyl pentane	19.	Xylene
7.	3-Methyl pentane	20.	<i>alpha</i> -Pinene
8.	Hexane	21.	Cyclohexanone
9.	Ethyl acetate	22.	<i>alpha</i> -Myrcene
10.	2-Methyl hexane	23.	D-Limonene
11.	Cyclohexane	24.	Phenol
12.	3-Methyl hexane	25.	Menthol
13.	Heptane	26.	2-Phenoxy ethanol

Conclusions

These results clearly demonstrate the fundamental sensitivity of the series 2 ULTRA-UNITY Air Toxics Analyzer configuration run with GC/MS. Quantitative detection of TO-17 air toxics ranging from methyl chloride to hexachloro-1,3-butadiene has been demonstrated down to 0.1 ppb on sorbent tubes, and even lower levels would be possible using the MS in SIM mode or sampling larger air volumes.

Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.

Reference

1. E. Hunter Daughtrey, K. D. Oliver, J. R. Adams, K. G. Kronmiller, W. A. Lonneman, W. A. McClenny. A comparison of sampling and analysis methods for low-ppbC levels of volatile organic compounds in ambient air. *J. Environ. Monit.* **2001**, *3*, 166-174.

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