

## Application Note 086

# Monitoring 'air toxics' in ambient air using sorbent tubes by automated, cryogen-free thermal desorption in accordance with US EPA Method TO-17

### Summary

This Application Note demonstrates the fundamental sensitivity of Markes' ULTRA-UNITY system for the analysis of TO-17 'air toxics' ranging in volatility from chloromethane to hexachlorobutadiene. Also highlighted is the ability of Markes' ClearView background-compensation software to improve signal-to-noise ratios and enhance spectral purity for trace-level compounds.

### Introduction

Volatile 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 chloromethane (methyl chloride) to hexachlorobutadiene and the trichlorobenzenes, and include polar as well as non-polar compounds. Several national and international standard methods have been developed for air toxics and related applications, including US EPA Method TO-17.

In response to increasing demand for measurement of ambient air toxics around the world, cryogen-free TD technologies have now been developed that offer an automated, method-compliant analytical platform for both tubes and canisters (for US EPA Method TO-15, see [Application Note 081](#)). The latest systems typically feature innovations such as repeat analysis for tubes, together with internal standard addition options for both canister and tube operation.

### Background to the TD-GC-MS analytical system

The analytical system used for this study comprised an ULTRA-UNITY™ thermal desorber, 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.

Extensive evaluation work had previously been carried out to determine the best combination of sorbents and trapping temperatures for the focusing trap. A combination of Tenax® TA, Carbograph™ 5TD and 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.

*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 vapours from the sample/sorbent tube to the focusing trap was completed (primary desorption), the trap was purged with dry carrier gas in the sampling direction to remove residual water. The flow of carrier gas was then reversed and the trap heated rapidly. At this point the retained organics were desorbed into the carrier gas stream and transferred/injected into the GC analytical column.

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

This project was carried out using two brands of 'purgeable volatiles' columns (A and B) and a mixed air toxic standard containing over 60 analytes, ranging in polarity and volatility.

### Experimental

#### Sample preparation:

A 62-component 1 ppm gas standard in nitrogen (Markes International part no. CGS15-1PPM), was used in combination with an air-actuated six-port Valco valve to inject 1 mL aliquots of standard gas, carried in pure nitrogen, into the sorbent tubes (see Figure 1).

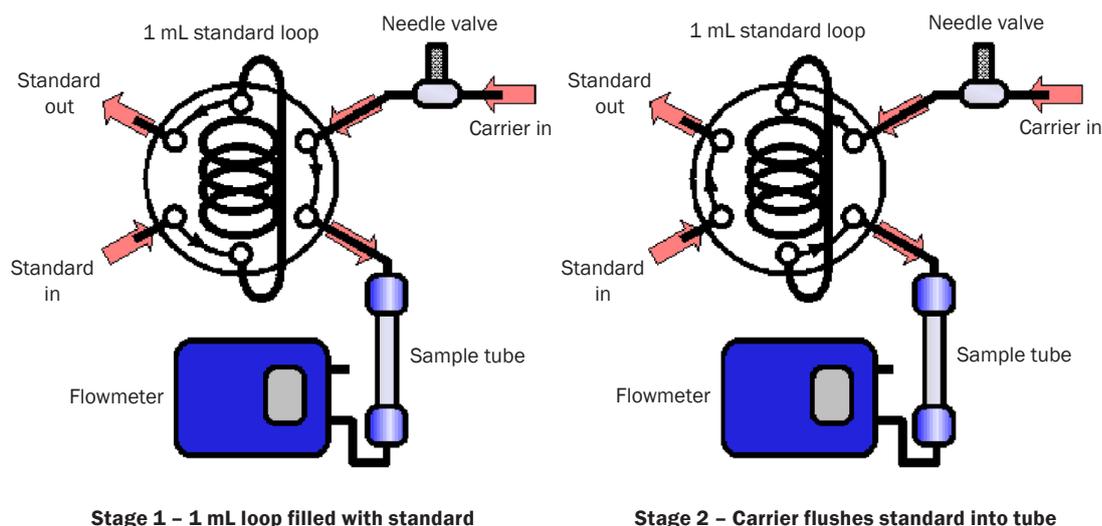
#### Sampling:

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 had been demonstrated to offer quantitative retention of air toxics, including the most volatile target compounds, from over 2 L<sup>†</sup> 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 also 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.

<sup>†</sup> Note that breakthrough volumes can be compromised by high humidity and/or by elevated ambient temperatures.



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

#### TD:

Instrument: UNITY (Markes International)  
 Focusing trap: Air Toxics Analyser/Soil Gas trap (Markes International part no. U-T15ATA-2S)  
 Tubes: Air Toxics Analyser (ATA) tubes (Markes International part no. C2-AXXX-5270) 'Universal' stainless steel tubes (Markes International part no. C3-AXXX-5266) packed with a combination of Tenax, Carbograph 1TD and Carboxen 1003.  
 Cold trap low temp.: 25°C  
 Tube desorb temp.: 320°C  
 Tube desorb time: 10 min  
 Trap purge time: 2.0 min  
 Cold trap high temp.: 320°C for 3 min  
 Split ratio: Splitless or 10:1 outlet split  
 Trap heating rate: 40°C/s  
 TD flow path: 140°C

#### GC:

Carrier gas: Helium  
 Columns A and B: 60 m × 0.32 mm × 1.80 µm  
 Mode: Constant pressure, 10 psi  
 Temp. program: 35°C (5 min), 5°C/min to 230°C (0 min)

#### MS:

MS source temp.: 230°C  
 MS quad temp.: 150°C  
 MSD transfer line: 200°C  
 Full scan: m/z 35–300

#### Software:

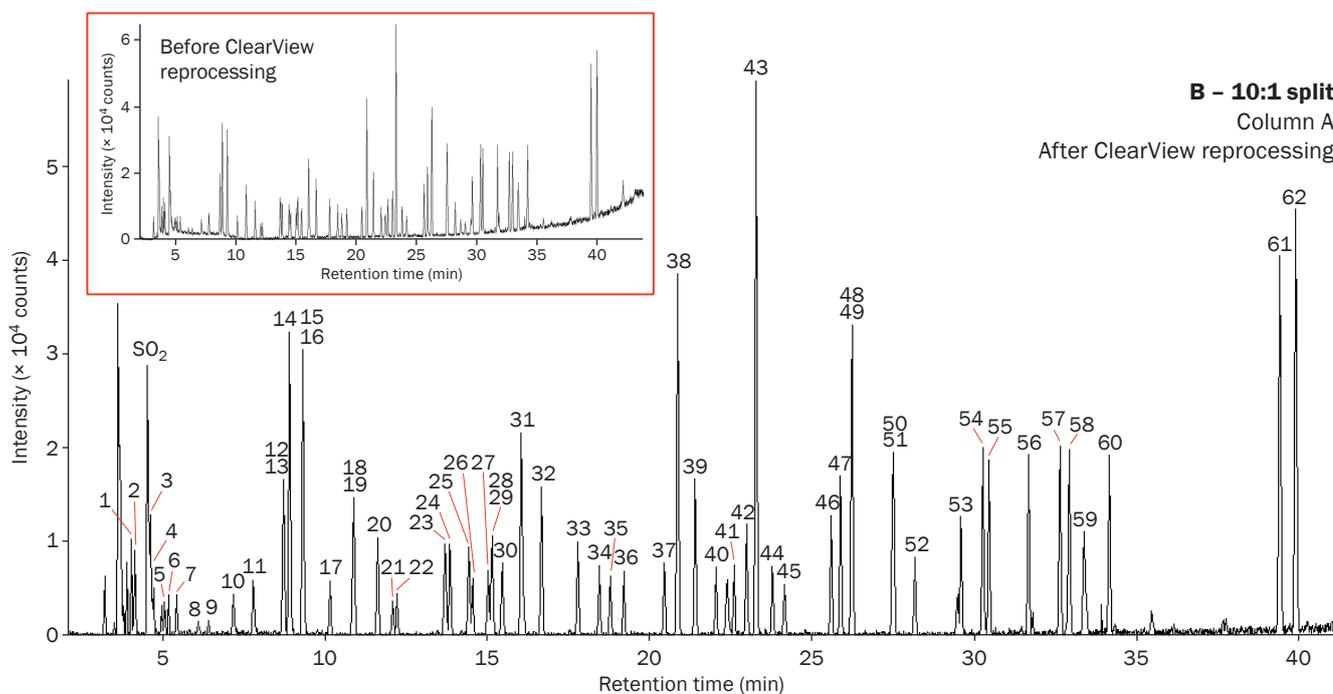
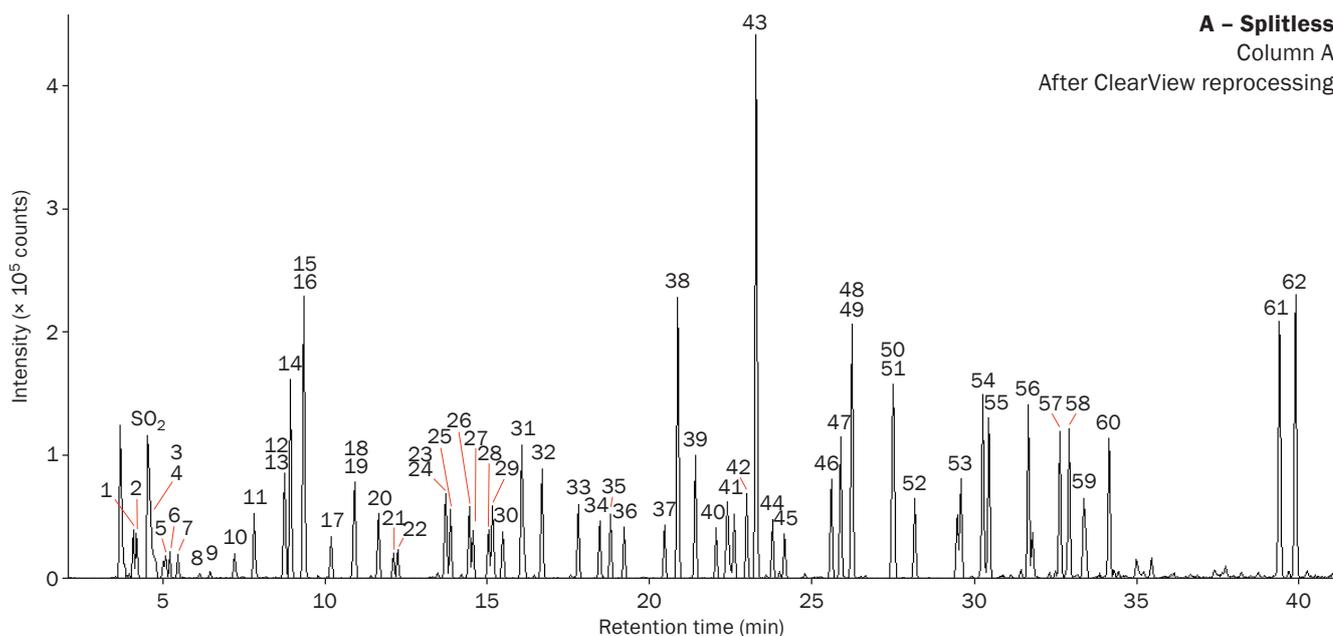
Post-run data processing with ClearView™ dynamic baseline compensation software was applied (see [Application Notes 083 and 085](#) for more details). Original data files were also retained.

#### Results and discussion

Figure 2A shows the chromatogram obtained for a sample equivalent to 1 L of 1 ppb standard, analysed splitless. Figure 2B shows the chromatogram obtained for a sample equivalent to 1 L of 1 ppb standard analysed with a 10:1 outlet split. The peak at 4.5 minutes is due to SO<sub>2</sub>, released from the carbon molecular sieve sorbent used at the back of the sampling tubes.

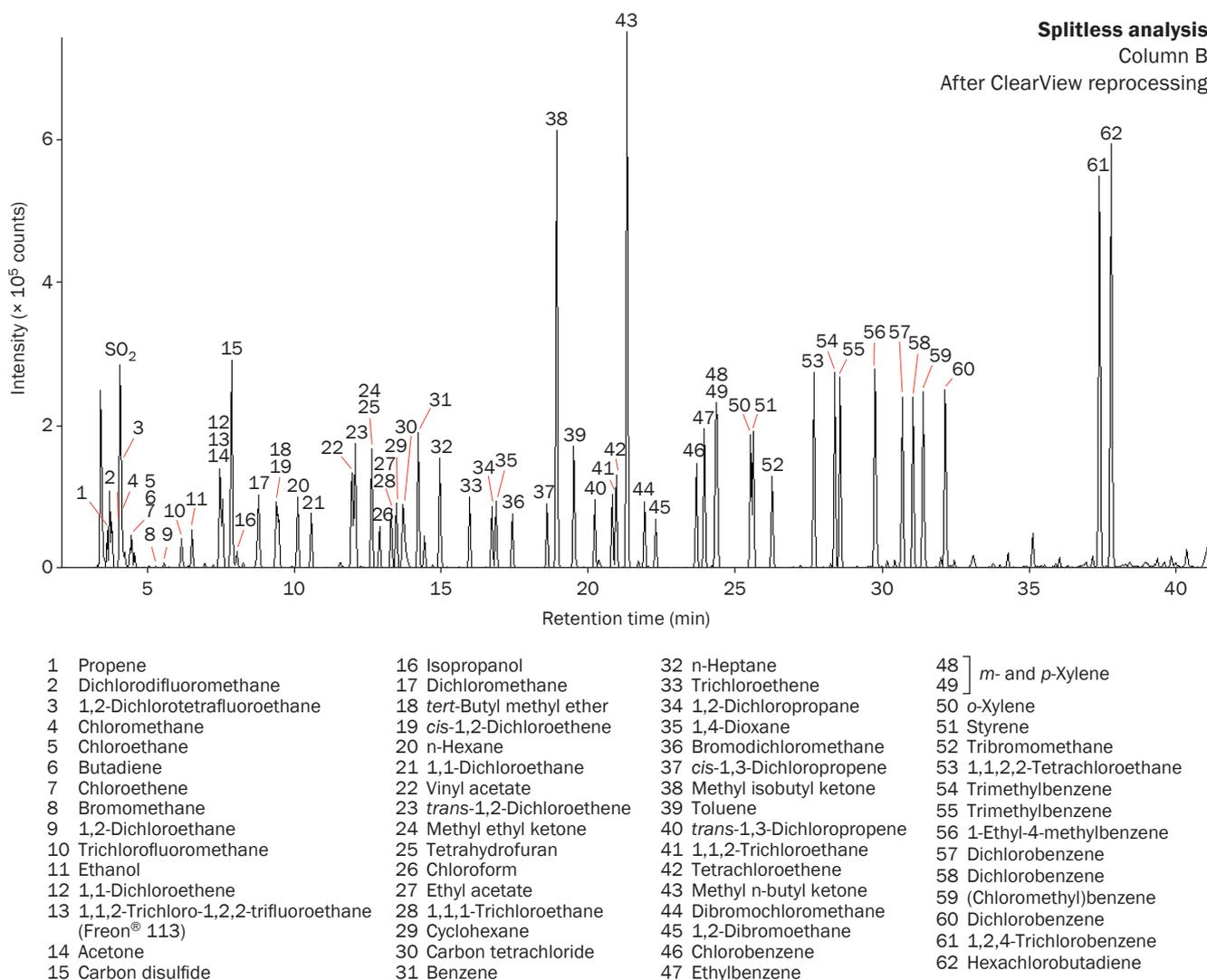
The GC–MS data shown in Figures 2A, 2B and 3 has been reprocessed using ClearView. Note the flatness of the baseline and lack of interferences/baseline anomalies. The original data were retained for comparative purposes, and an example is shown in the inset of Figure 2B.

Note that no peak-related information was impacted by application of ClearView, but that both signal-to-noise ratios (sensitivity) and spectral purity were enhanced in the reprocessed data (Figure 4).

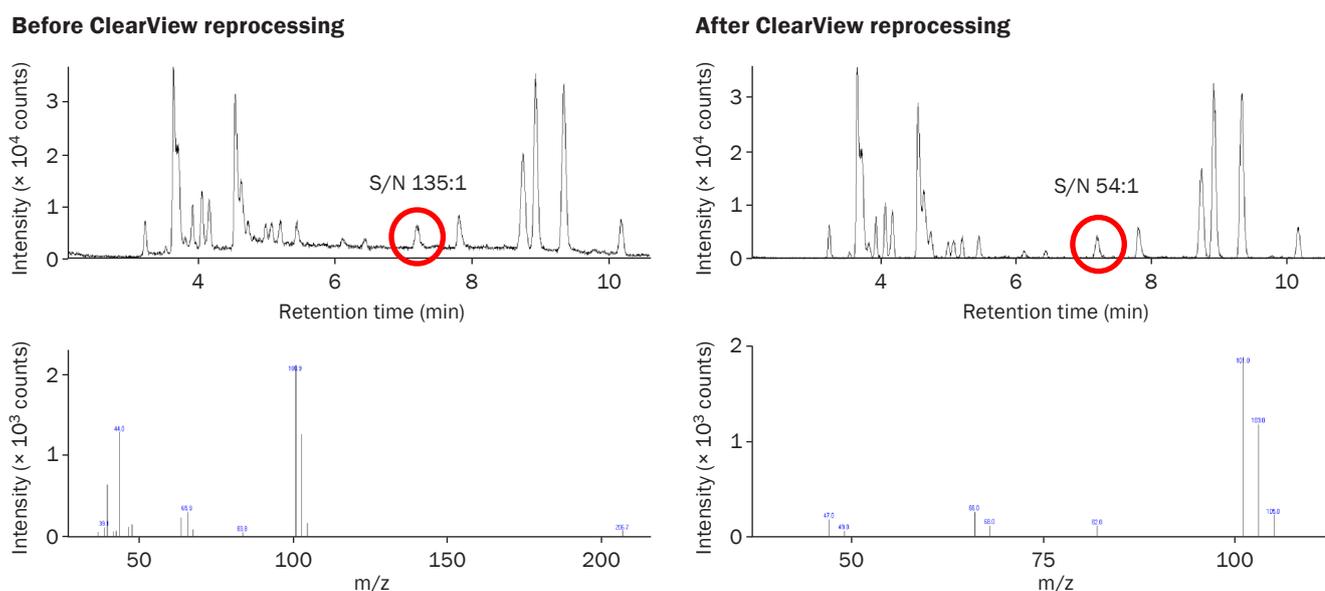


1 Propene	16 Isopropanol	32 n-Heptane	48 ] <i>m</i> - and <i>p</i> -Xylene
2 Dichlorodifluoromethane	17 Dichloromethane	33 Trichloroethene	49 ] <i>m</i> - and <i>p</i> -Xylene
3 1,2-Dichlorotetrafluoroethane	18 <i>tert</i> -Butyl methyl ether	34 1,2-Dichloropropane	50 <i>o</i> -Xylene
4 Chloromethane	19 <i>cis</i> -1,2-Dichloroethene	35 1,4-Dioxane	51 Styrene
5 Chloroethane	20 n-Hexane	36 Bromodichloromethane	52 Tribromomethane
6 Butadiene	21 1,1-Dichloroethane	37 <i>cis</i> -1,3-Dichloropropene	53 1,1,2,2-Tetrachloroethane
7 Chloroethene	22 Vinyl acetate	38 Methyl isobutyl ketone	54 Trimethylbenzene
8 Bromomethane	23 <i>trans</i> -1,2-Dichloroethene	39 Toluene	55 Trimethylbenzene
9 1,2-Dichloroethane	24 Methyl ethyl ketone	40 <i>trans</i> -1,3-Dichloropropene	56 1-Ethyl-4-methylbenzene
10 Trichlorofluoromethane	25 Ethyl acetate	41 1,1,1-Trichloroethane	57 Dichlorobenzene
11 Ethanol	26 Tetrahydrofuran	42 Tetrachloroethene	58 Dichlorobenzene
12 1,1-Dichloroethene	27 Chloroform	43 Methyl <i>n</i> -butyl ketone	59 (Chloromethyl)benzene
13 1,1,1,2-Trichloro-1,2,2-trifluoroethane (Freon® 113)	28 1,1,1-Trichloroethane	44 Dibromochloromethane	60 Dichlorobenzene
14 Acetone	29 Cyclohexane	45 1,2-Dibromoethane	61 1,2,4-Trichlorobenzene
15 Carbon disulfide	30 Carbon tetrachloride	46 Chlorobenzene	62 Hexachlorobutadiene
	31 Benzene	47 Ethylbenzene	

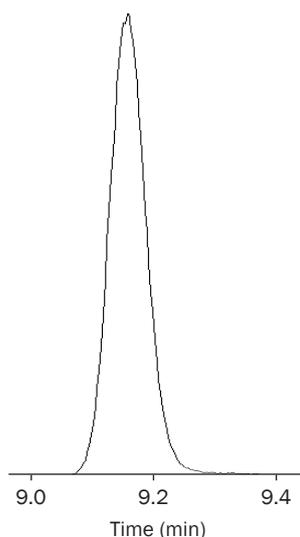
**Figure 2:** Analysis of a sample equivalent to 1 L of a 1 ppb standard using Column A, following reprocessing by ClearView, (**A**) splitless, and (**B**) with a 10:1 outlet split. The inset shows the same data before ClearView processing – note the minor baseline anomaly early in the run due to residual water, and increasing column bleed and noise as the GC oven reaches its top temperature.



**Figure 3:** Splitless analysis of a sample equivalent to 1 L of a 2 ppb standard using Column B, following reprocessing by ClearView.



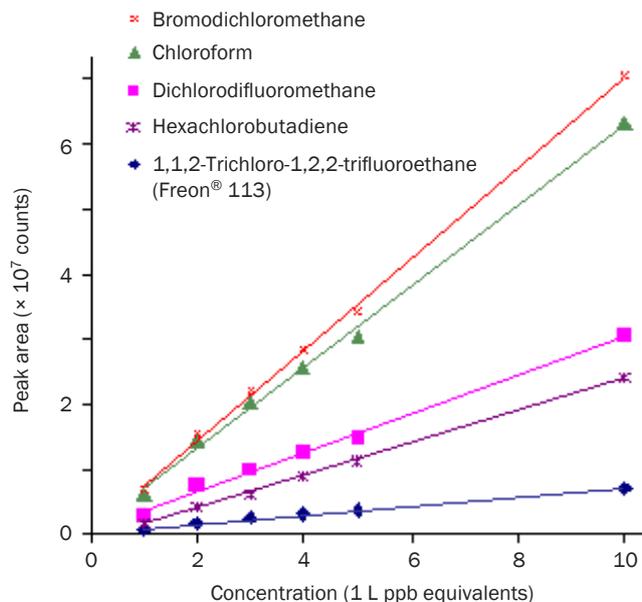
**Figure 4:** Expanded portions of Figure 2B, showing the enhancement of spectral purity and signal-to-noise ratios for trichlorofluoromethane (circled) using ClearView.



**Figure 5:** Peak shape for isopropanol (extracted ion  $m/z$  45) at 1 ppb, analysed splitless using ATA tubes and Column A.

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 isopropanol (Figure 5).

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 be readily achieved by using the mass spectrometer in selected ion monitoring (SIM) mode.

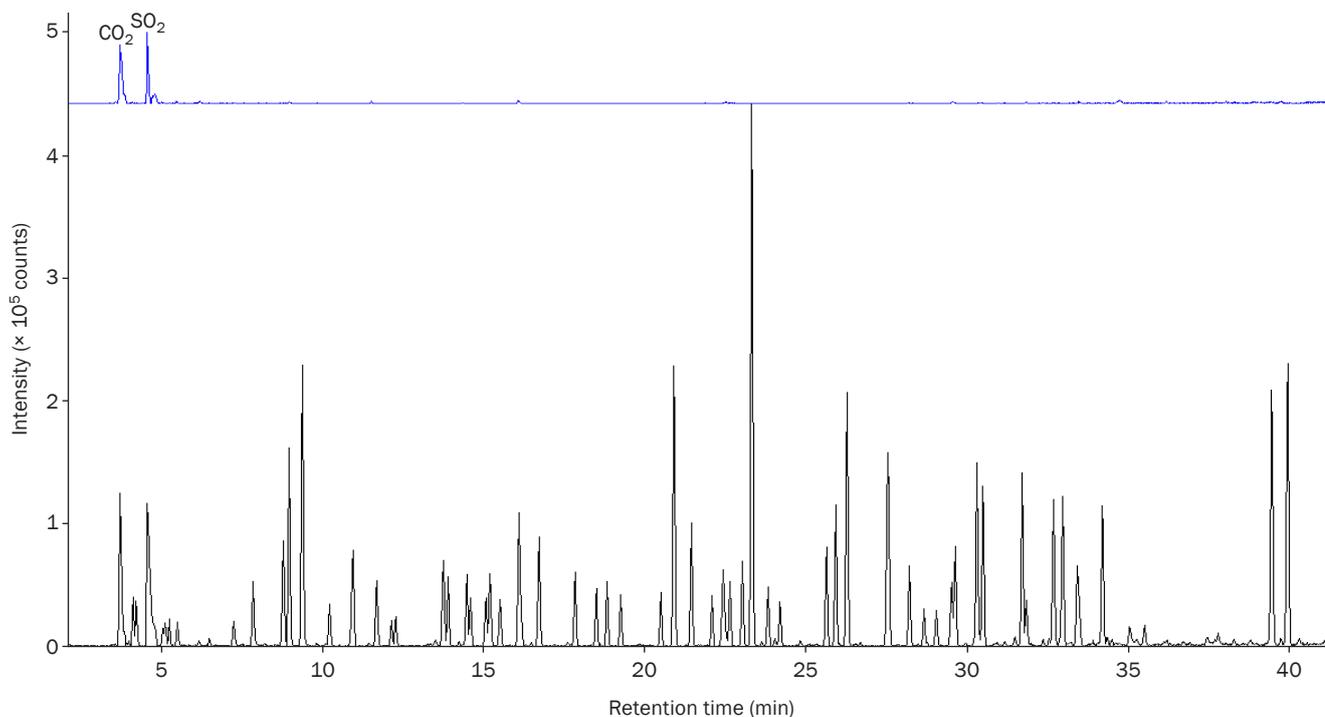


**Figure 6:** Linearity plots from 1 to 10 ppb.

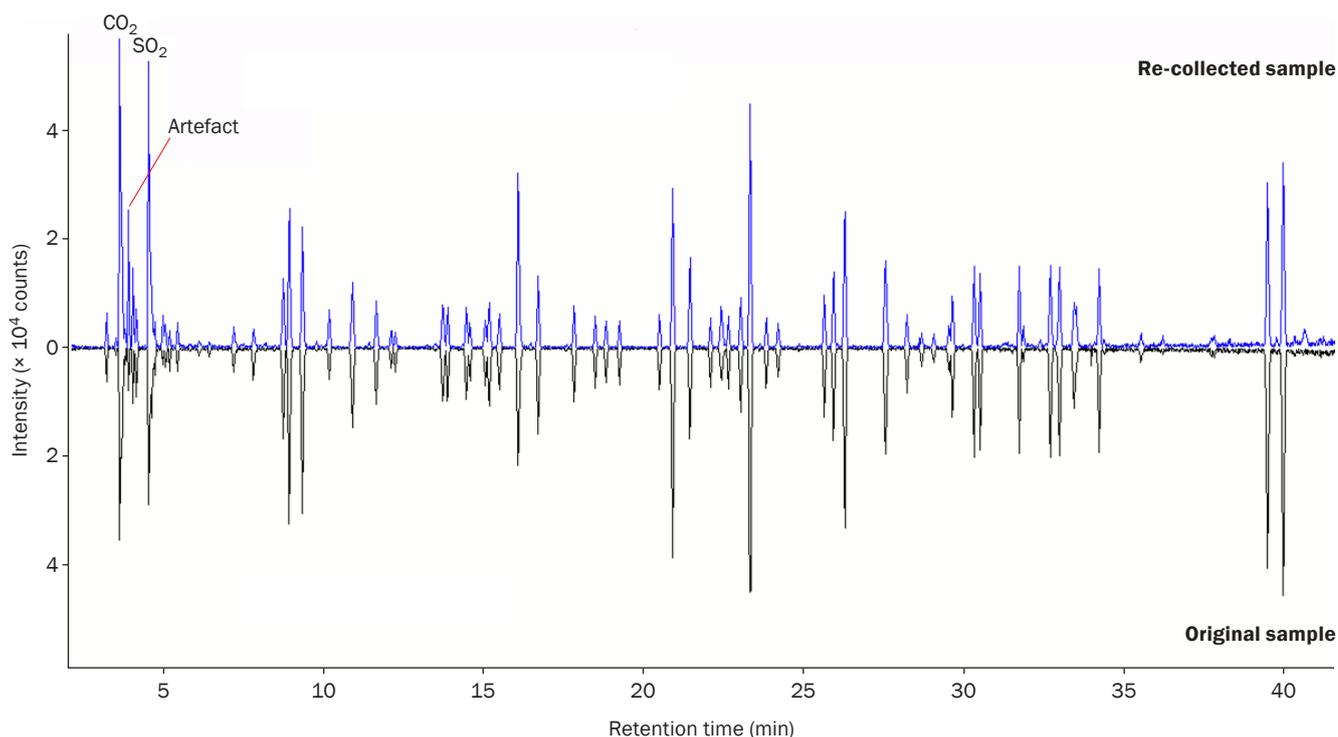
### Linearity

Figure 6 illustrates system linearity under splitless conditions using Column A, with  $R^2$  values of 0.99 for 1,1,2-trichloro-1,2,2-trifluoroethane (Freon® 113), dichlorodifluoromethane, chloroform, bromodichloromethane and hexachlorobutadiene. Similar results were obtained using Column B.

Carryover for 1 L of 10 ppb standard analysed splitless, using Column A, was less than 0.5% (see Figure 7).



**Figure 7:** Carryover (top, blue) at <0.5% from 1 L of a 10 ppb standard (bottom, black), analysed splitless using ATA tubes and Column A.



**Figure 8:** Results of re-collection and repeat analysis (top, blue) compared to the original analysis (bottom, black) of a 1 ppb standard (bottom, black), analysed with a 10:1 outlet split using ATA tubes and Column A.

The ability to quantitatively re-collect split flow (SecureTD-Q™) facilitates repeat analysis and validation of TO-17 methods/data. The repeat analysis of a sample equivalent to 1 L of 1 ppb air toxics standard, split 10:1 (Figure 8), and analysed using Column A 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 run under splitless conditions using Column A. RSD values for eight compounds, covering the volatility and polarity range of the standard, are shown in Table 1. Typical RSDs were less than 6%.

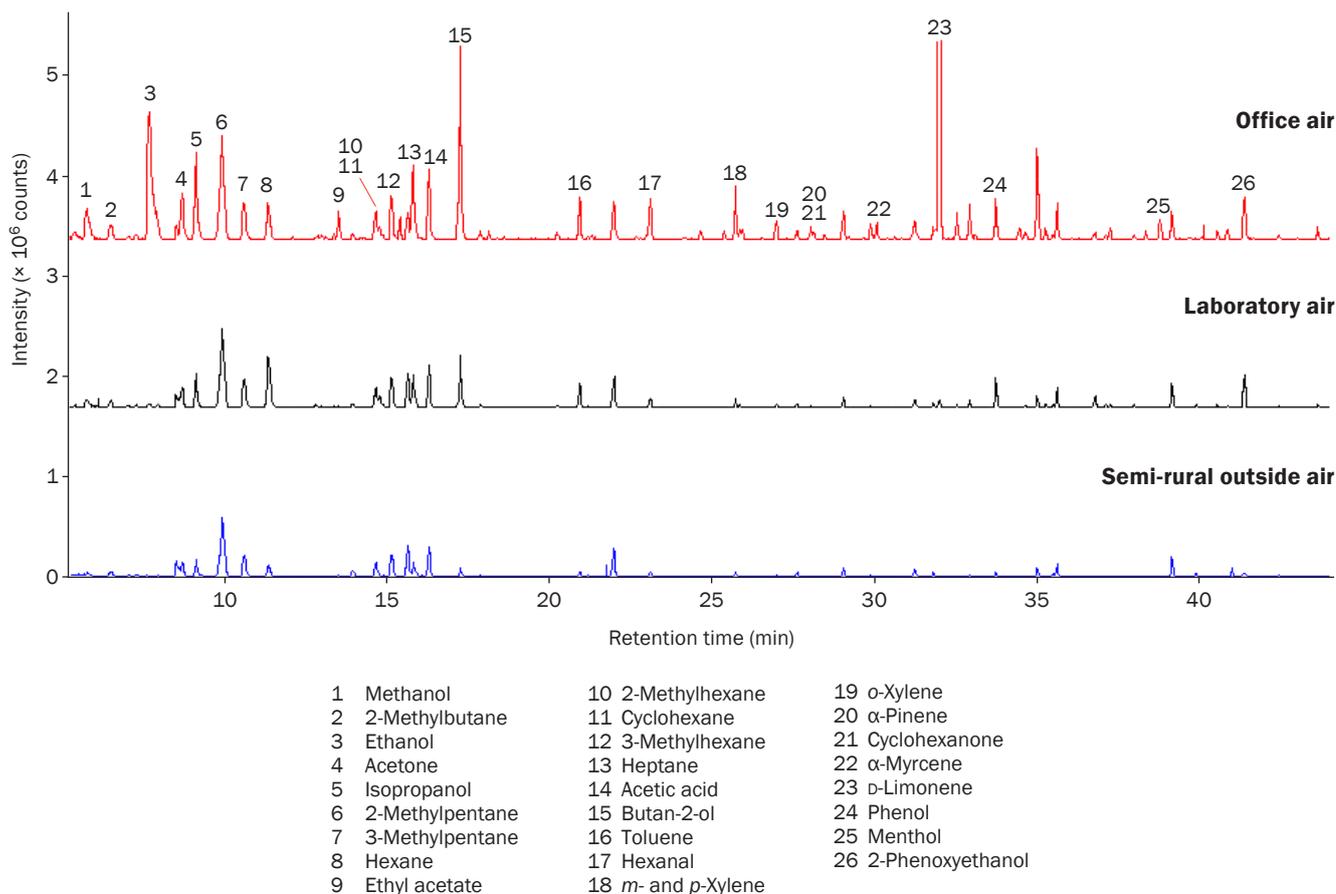
Compound	RSD (%)
Dichlorodifluoromethane	2.8
Butadiene	5.5
Dichloromethane	3.4
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon® 113)	1.8
Chloroform	1.8
Benzene	6.0
Toluene	1.7
Hexachlorobutadiene	3.8

**Table 1:** System reproducibility demonstrated using eight compounds covering a typical range of 'air toxic' volatilities and polarities (n = 6), using ATA tubes and Column A under splitless conditions.

### 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 min, giving a total volume of 1 L in each case.

Three different ambient locations were sampled: office, laboratory and semi-rural outside air. Each sample tube was analysed splitless using Column A and a full-scan MS method from m/z 10–300. The data was processed using ClearView and overlaid (Figure 9).



**Figure 9:** Analysis of three 1 L air samples collected using 'Universal' sorbent tubes and desorbed splitless using Column A.

## Conclusions

These results clearly demonstrate the fundamental sensitivity of the ULTRA-UNITY Air Toxics Analyser configuration run with GC-MS. Quantitative detection of TO-17 'air toxics' ranging from chloromethane to hexachlorobutadiene has been demonstrated down to 0.1 ppb on sorbent tubes, and even lower levels would be possible by using the mass spectrometer in SIM mode and/or sampling larger air volumes.

This work also demonstrates the benefits of ClearView reprocessing software for reducing interferences; both in terms of improving signal-to-noise ratios and enhancing spectral purity for trace compounds.

## References

1. E. Hunter Daughtrey *et al.*, A comparison of sampling and analysis methods for low-ppbC levels of volatile organic compounds in ambient air, *Journal of Environmental Monitoring*, 2001, 3: 166-174, <http://dx.doi.org/10.1039/B007158G>.

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