Thermal Desorption Technical Support

Note 86: EPA Method TO-17 for monitoring 'air toxics' in ambient air using sorbent tubes and automated, cryogen-free thermal desorption

Key Words:

Environmental, Tube, TO-17, Air monitoring

Introduction

Volatile (vapour-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 & trichlorobenzenes and include polar as well as apolar 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 around the world, cryogen-free TD technologies have now been developed which offer an automated, method-compliant analytical platform for both tubes and canisters (for US EPA method TO-15, see TDTS 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™ thermal desorber (TD) (see 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 UNITY 2.

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®, Carbopack X™ and Carboxen™ 1003 sorbents held at a trapping temperature of 25ºC was ultimately found to work best, offering both quantitative recovery of target compounds and selective elimination of water.

Figure 1: ULTRA-UNITY 2

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 2 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.

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 had been demonstrated to offer quantitative retention of air toxics, including the most volatile target compounds, from over 2 L* of air at 25ºC. 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.

**Note that breakthrough volumes can be compromised by high humidity and/or by elevated ambient temperatures.*

Analytical conditions

This project was carried out using two 'purgeable volatiles' column brands and a mixed air toxic standard containing over 60 analytes, ranging in polarity and volatility.

UNITY 2 parameters

Cold Trap: Markes Air Toxic Analyser/Soil Gas trap (part no. U-T15ATA-2S)

Tubes: Markes Air Toxics Analyser (ATA) tubes (part no. C2-AXXX-5270)

Markes 'Universal' stainless steel tubes (part no. C3-AXXX-5266) packed with a combination of Tenax, Carbograph 1TD and Carboxen 1003.

Cold trap low temp.: 25°C

Tube desorption temp.: 320°C

Tube desorption 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 parameters

Carrier gas: He

Columns A and B: 60 m x 0.32 mm x 1.80 µm

Constant pressure mode: 10 psi

Temp. program: 35°C (5 min), 5°C/min to 230°C (0 min)

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

Post-run data processing with ClearView™ 'dynamic background compensation' software was applied (see Markes TDTS 83 and TDTS 85 for more details). Original data files were also retained.

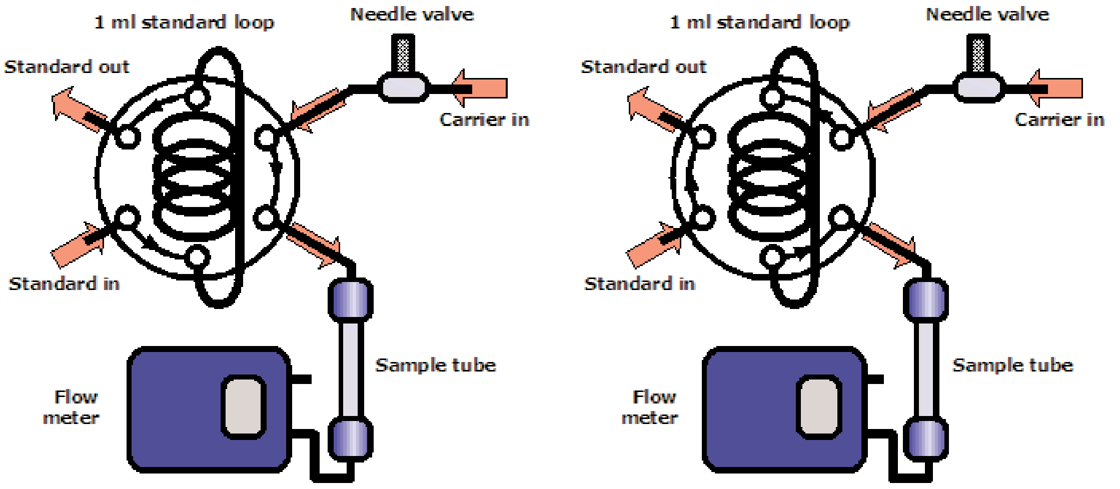
Sample preparation

A 62 component 1 ppm gas standard in nitrogen, available from Markes International (part no. CGS15-1PPM), was used in combination with an air actuated 6 port Valco® valve to inject 1 ml aliquots of standard gas, carried in pure nitrogen, into the sorbent tubes (see figure 2).

Results

Figure 3a shows the chromatogram obtained for a sample equivalent to 1 L of 1 ppb standard analysed splitless. Figure 3b 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_2, released from the carbon molecular sieve sorbent used at the back of the sampling tubes.

The GC/MS data shown in figures 3a, 3b and 4 have 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 figure 3c.



Stage 1 – 1 ml loop filled with standard

Stage 2 – Carrier flushes standard into tube

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

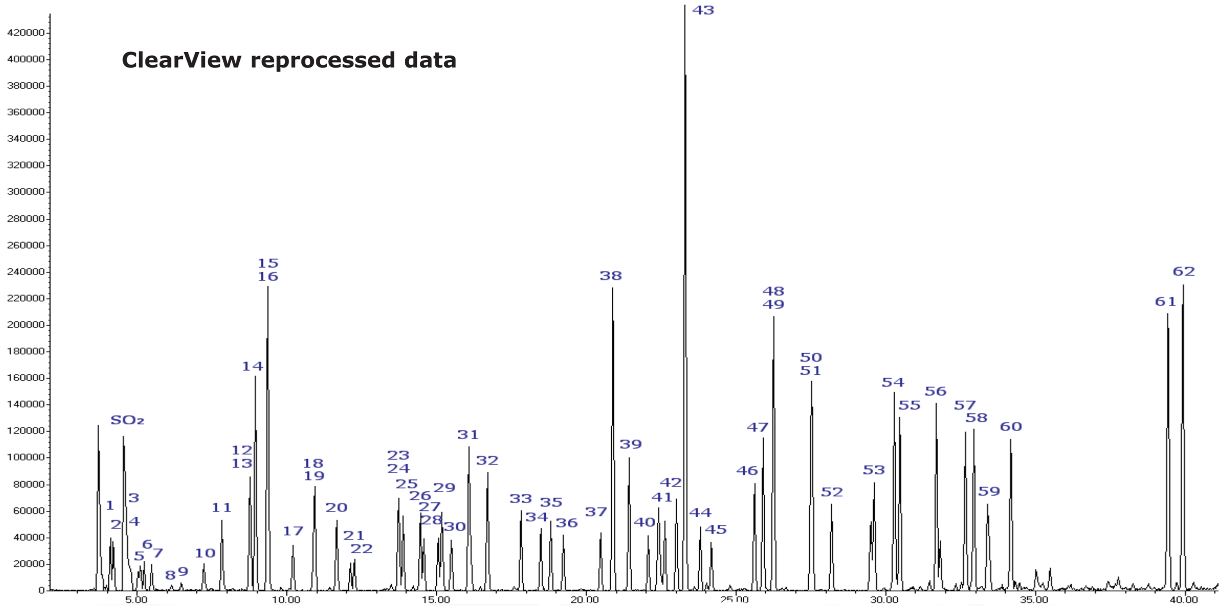


Figure 3a: Sample equivalent to 1 L of a 1 ppb standard analysed splitless using ATA tubes and column A

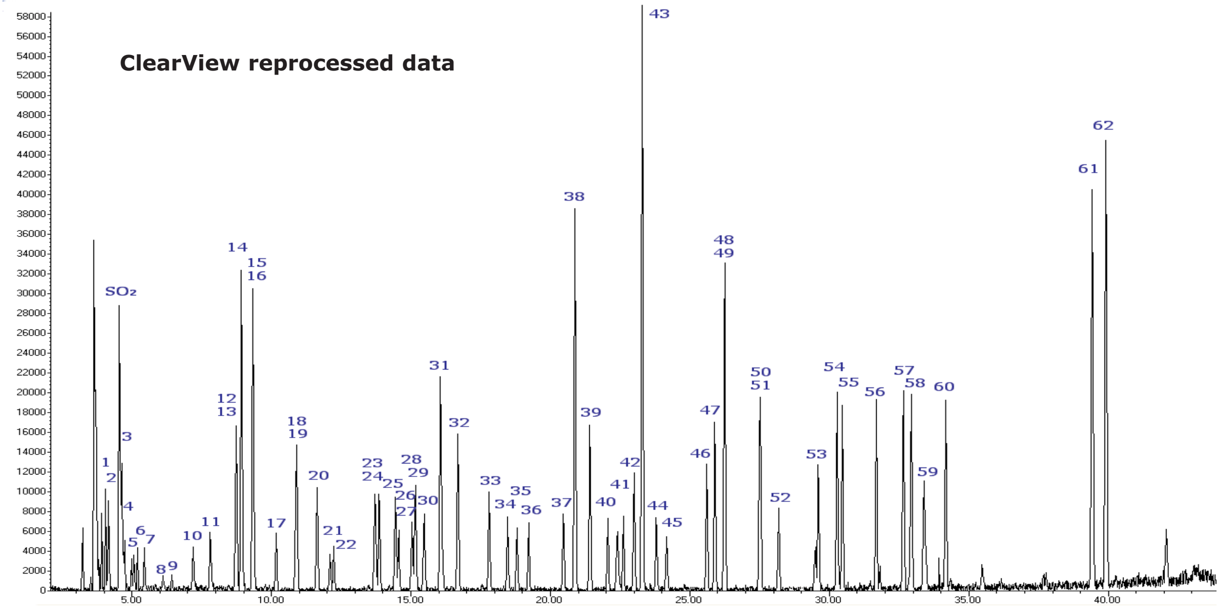


Figure 3b: Sample equivalent to 1 L of a 1 ppb standard analysed with a 10:1 split using ATA tubes and column A

1	Propylene
2	Dichlorodifluoromethane
3	1,2-Dichlorotetrafluoroethane
4	Methyl chloride
5	Chloroethane
6	1,3-Butadiene
7	Vinyl chloride
8	Methyl bromide (bromomethane)
9	1,2-Dichloroethane
10	Trichlorotrifluoroethane (Freon® 113)
11	Ethanol
12	1,1-Dichloroethylene
13	1,1,2-Trichlorotrifluoroethane
14	Acetone
15	Carbon disulfide
16	Isopropyl alcohol
17	Methylene chloride
18	Tert-butyl methyl ether
19	Cis-1,2-dichloroethylene
20	n-Hexane
21	1,1-Dichloroethane
22	Vinyl acetate
23	Trans-1,2-dichloroethylene
24	Methyl ethyl ketone
25	Ethyl acetate
26	Tetrahydrofuran
27	Chloroform
28	1,1,1-Trichloroethane
29	Cyclohexane
30	Carbon tetrachloride
31	Benzene
32	n-Heptane
33	Trichloroethylene
34	1,2-Dichloropropane
35	1,4-Dioxane
36	Bromodichloromethane
37	Cis-1,3-dichloropropene
38	Methyl isobutyl ketone
39	Toluene
40	Trans-1,3-Dichloropropene
41	1,1,2-Trichloroethane
42	Tetrachloroethylene
43	Methyl n-butyl ketone
44	Dibromochloromethane
45	1,2-Dibromoethane
46	Chlorobenzene
47)	
48)	*o*-, *m*-, *p*-Xylene
49)	+ ethylbenzene
50)	
51	Styrene
52	Tribromomethane
53	1,1,2,2-Tetrachloroethane
54	Trimethylbenzene
55	Trimethylbenzene
56	1-Ethyl-4-methyl benzene
57	Dichlorobenzene
58	Dichlorobenzene
59	Chloromethylbenzene (alpha)
60	Dichlorobenzene
61	1,2,4-Trichlorobenzene
62	Hexachloro-1,3-butadiene

Table 1: Elution order for the air toxics standard run on column A

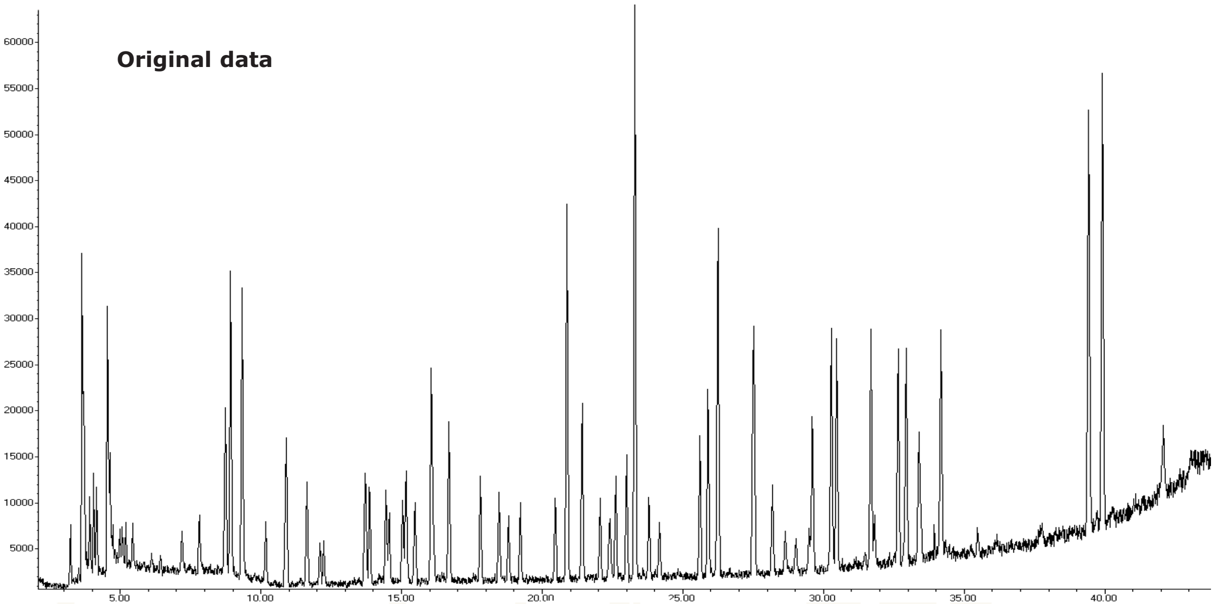


Figure 3c: 1 L of a 1 ppb air toxics standard as shown in figure 3b, but without ClearView reprocessing. Note minor baseline anomaly due to residual water early in the run and increasing column bleed and noise as the GC oven reaches its top temperature

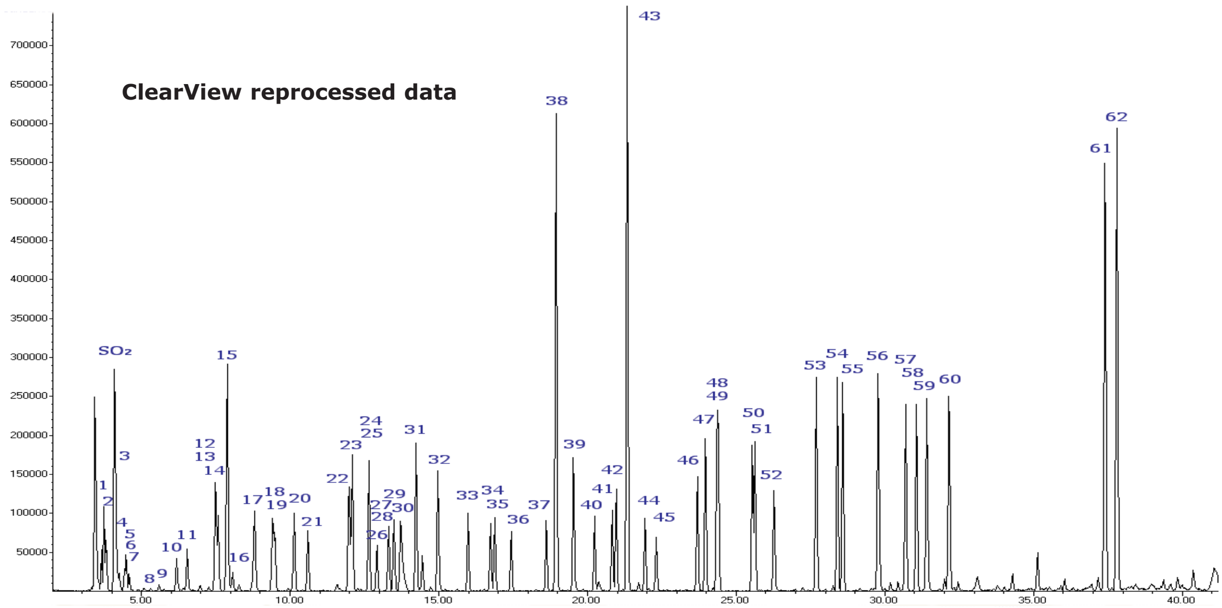


Figure 4: Sample equivalent to 1 L of a 2 ppb standard analysed splitless using ATA tubes and column B

1	Propylene
2	Dichlorodifluoromethane
3	1,2-Dichlorotetrafluoroethane
4	Methyl chloride
5	Chloroethane
6	Vinyl chloride
7	1,3-Butadiene
8	Methyl bromide (bromomethane)
9	1,2-Dichloroethane
10	Trichlorotrifluoroethane (Freon® 113)
11	Ethanol
12	1,1-Dichloroethylene
13	1,1,2-Trichlorotrifluoroethane
14	Acetone
15	Carbon disulfide
16	Isopropyl alcohol
17	Methylene chloride
18	Tert-butyl methyl ether
19	Cis-1,2-dichloroethylene
20	n-Hexane
21	1,1-Dichloroethane
22	Vinyl acetate
23	Trans-1,2-dichloroethylene
24	Methyl ethyl ketone
25	Tetrahydrofuran
26	Chloroform
27	Ethyl acetate
28	1,1,1-Trichloroethane
29	Cyclohexane
30	Carbon tetrachloride
31	Benzene
32	n-Heptane
33	Trichloroethylene
34	1,2-Dichloropropane
35	1,4-Dioxane
36	Bromodichloromethane
37	Cis-1,3-Dichloropropene
38	Methyl isobutyl ketone
39	Toluene
40	Trans-1,3-Dichloropropene
41	1,1,2-Trichloroethane
42	Tetrachloroethylene
43	Methyl n-butyl ketone
44	Dibromochloromethane
45	1,2-Dibromoethane
46	Chlorobenzene
47)	*o*-, *m*-, *p*-Xylene + ethylbenzene
48)	
49)	
50)	
51	Styrene
52	Tribromomethane
53	1,1,2,2-Tetrachloroethane
54	Trimethylbenzene
55	Trimethylbenzene
56	1-Ethyl-4-methyl benzene
57	Dichlorobenzene
58	Dichlorobenzene
59	Chloromethylbenzene (alpha)
60	Dichlorobenzene
61	1,2,4-Trichlorobenzene
62	Hexachloro-1,3-butadiene

Table 2: Elution order for the air toxics standard run on column B

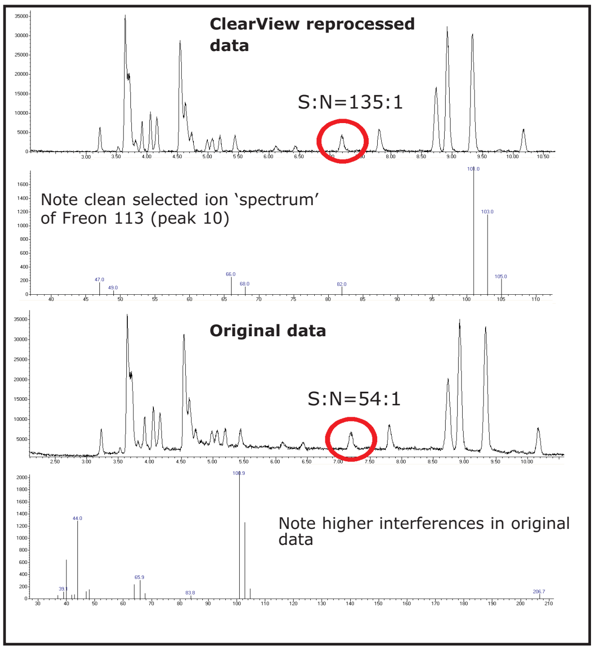


Figure 5: Expanded portions of the air toxics standard analysed split (figure 3b and 3c) showing ClearView enhancement of spectral purity and signal:noise

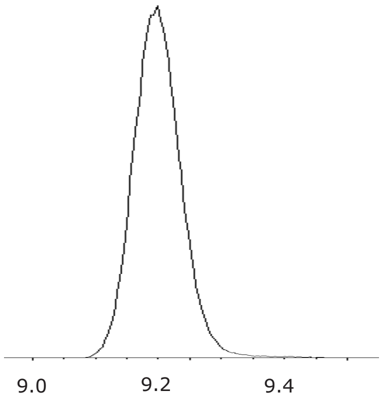


Figure 6: Peak shape for IPA at 1 ppb analysed splitless using ATA tubes and column A, extracted mass ion 45

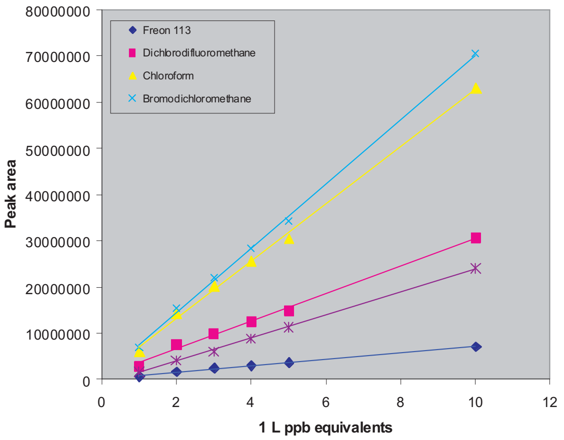


Figure 7: Linearity plots from 1 to 10 ppb standards collected using ATA tubes and analysed splitless

Note that no peak-related information was impacted by application of ClearView but that both signal: noise ratios (sensitivity) and spectral purity were enhanced in the reprocessed data (figure 5).

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).

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 MS in Selected Ion Monitoring (SIM) mode.

Linearity

Figure 7 illustrates system linearity under splitless conditions using column A with R^2 values of 0.99 for trichlorotrifluoroethane (Freon® 113), dichlorodifluoromethane, chloroform, bromodichloromethane and hexachloro-1,3-butadiene. 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 8).

SecureTD-Q™: Quantitative re-collection 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), 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. Example % Relative Standard Deviation (RSD) for 8 compounds, covering the volatility and polarity range of the standard, are shown in table 3. Typical RSDs were less than 6%.

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.

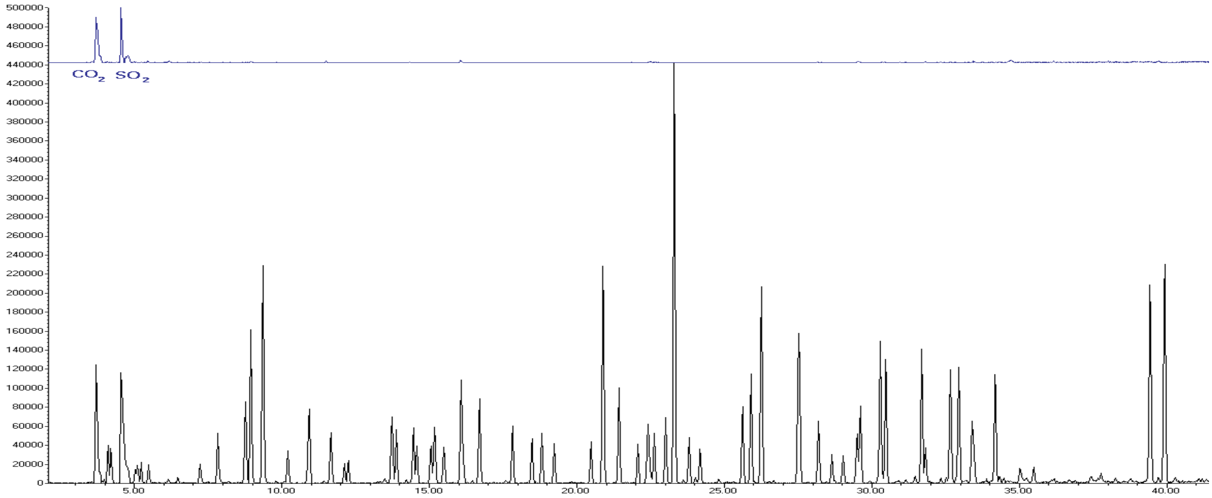


Figure 8: Carryover (blue) < 0.5% from 1 L 1 ppb standard (black) analysed splitless using ATA tubes and column A

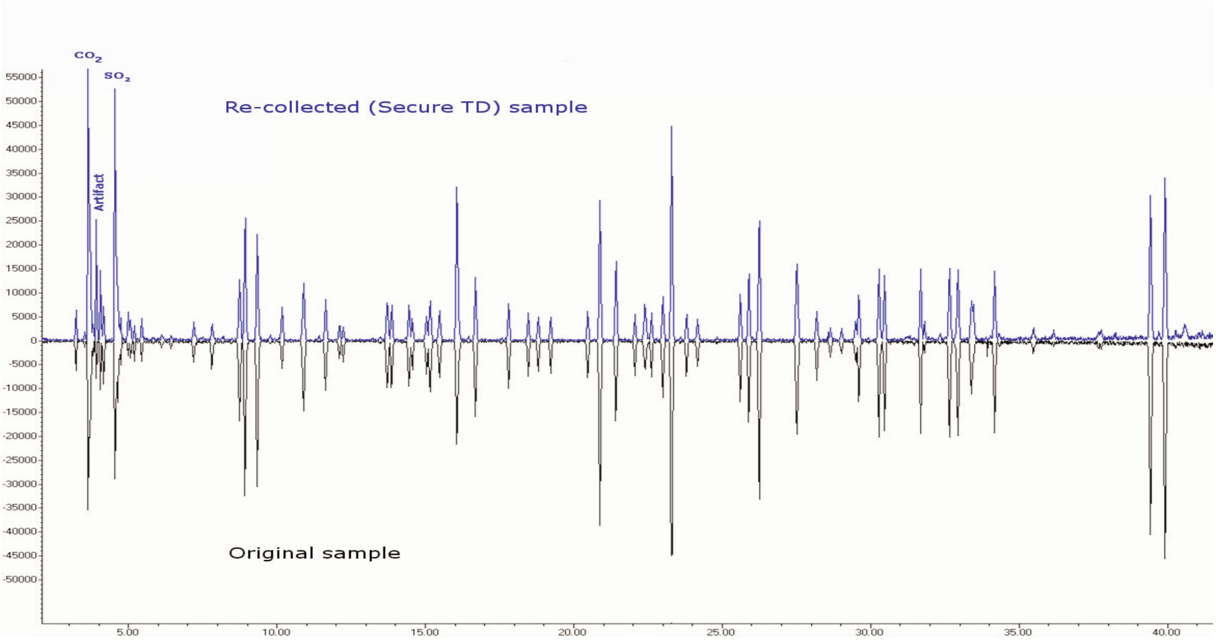


Figure 9: Re-collection and repeat analysis results from a 1 ppb standard analysed using ATA tubes, column A and a 10:1 outlet split

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

Table 3: System reproducibility demonstrated using 8 compounds covering a typical range of 'air toxic' volatilities and polarities (n=6). Conditions: ATA tubes, column A, splitless

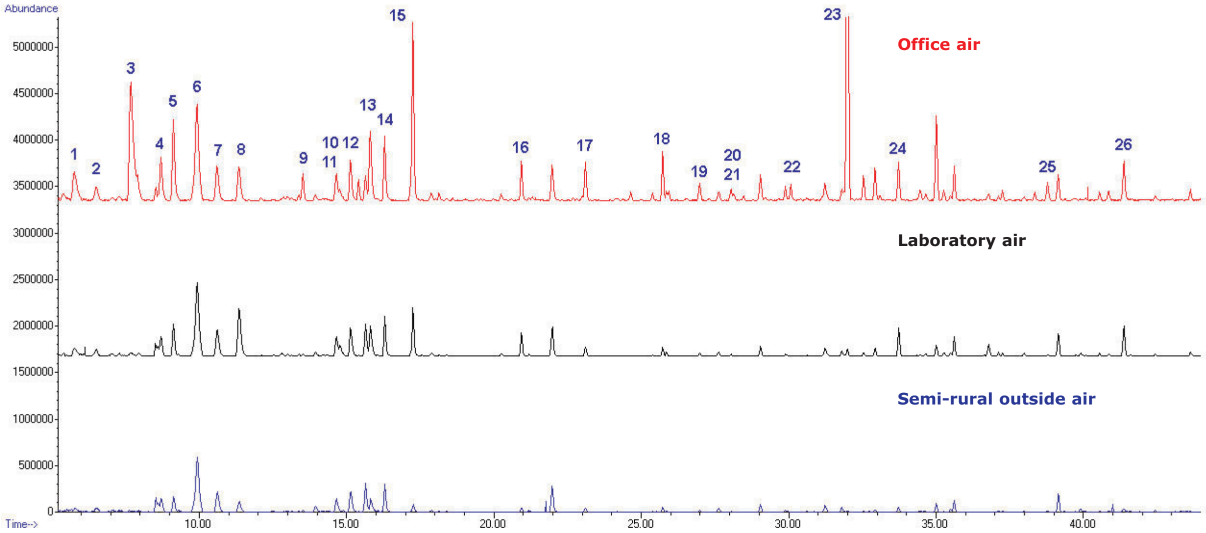


Figure 10: Chromatograms from three 1 L real air samples collected using 'Universal' sorbent tubes and desorbed splitless using column A

1	Methanol	10	2-Methyl hexane	19	Xylene
2	2-Methyl butane	11	Cyclohexane	20	Alpha-pinene
3	Ethanol	12	3-Methyl hexane	21	Cyclohexanone
4	Acetone	13	Heptane	22	Alpha-myrcene
5	Isopropyl alcohol	14	Acetic acid	23	D-limonene
6	2-Methyl pentane	15	1-Methyl-2-propanol	24	Phenol
7	3-Methyl pentane	16	Toluene	25	Menthol
8	Hexane	17	Hexanal	26	2-Phenoxy ethanol
9	Ethyl acetate	18	Xylene		

Table 4: Selected compounds detected from 3 real air samples, run splitless

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 10 - 300 amu. The data were processed using ClearView and overlaid (figure 10).

Conclusions

These results clearly demonstrate the fundamental sensitivity of the series 2 ULTRA UNITY Air Toxics Analyser 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 by using the MS 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:noise and enhancing spectral purity for trace compounds.

Trademarks

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References

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