Thermal Desorption Technical Support

Note 81: Analysis of canister air samples using cryogen-free thermal desorption in compliance with US EPA method TO-15

Key Words:

Environmental, Canister, TO-15, Air monitoring, Air toxics

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 methylchloride to hexachlorobutadiene & trichlorobenzenes and include some 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-15 (Determination of volatile organic compounds in air collected in SUMMA® canisters and analyzed by GC/MS).

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 canisters and sorbent tubes (for US EPA Method TO-17, see TDTS 86). 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 UNITY 2™ thermal desorber (TD) and Canister Interface Accessory (CIA 8) coupled to a GC/MS (see figure 1).

Using this TO-15 compliant system, controlled volumes of canister air/gas were transferred to an electrically-cooled, sorbent-packed focusing trap inside UNITY 2.

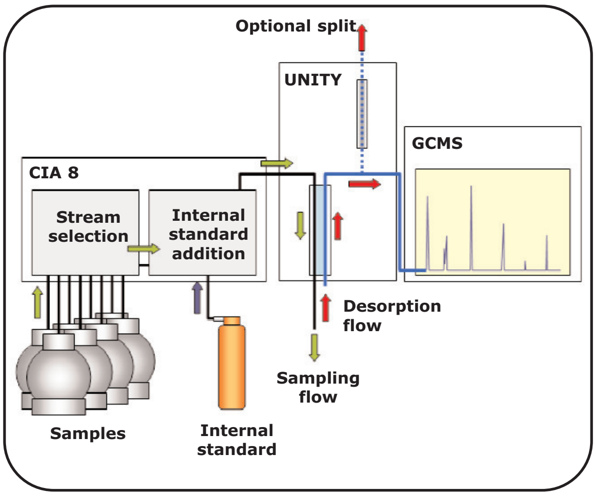

Figure 1: CIA 8-UNITY 2-GC/MS schematic

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.

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 canister to the focusing trap was completed, 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 may be transferred to the analytical column in a narrow band of vapour ensuring optimum sensitivity.

Analytical conditions

This project was carried out using 3 different columns and under slightly different analytical conditions (see A, B and C below) as a check for robustness. Mixed air toxic standards containing over 60 analytes, ranging in polarity and volatility, were used for the experiments.

CIA 8-TD parameters

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

Cold trap low temp.: 25°C

Line purge: 1.0 min

Trap purge time: 2.0 min

Cold trap high temp: 320°C for 3 min

Split ratio: (A & C) splitless (B) 4:1 'outlet' split

Trap heating rate: 40°C/s

TD flow path: 140°C

GC parameters

Carrier gas: He

Column A: 60 m x 0.32 mm x 1.80 µm column for purgeable volatiles

Column B: 60 m x 0.32 mm x 1.0 µm bonded methyl silicone phase

Column C: 60 m x 0.32 mm x 1.80 µm column for purgeable volatiles

Constant pressure mode: 10 psi

Temp. programmes used for each column:

(A) 40°C (5 min), 5°C/min to 230°C (0 min)

(B) 35°C (3 min), 5°C/min to 115°C, 10°C/min to 180°C, 20°C/min to 240°C (0 min)

(C) 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

Column A Full scan 35 - 300 amu

Post-run data processing with ClearView™ 'dynamic background compensation' (DBC) software was applied to some of the GCMS data obtained (see TDTS 83 and 85 for more details). Original data files were also retained.

Sample preparation

62 component 1 ppm TO-15 gas standards in nitrogen were used to fill a 5 L Silcosteel™ canister to 5 psi. Each standard was connected to the canister *via* a short length of 1/8" stainless steel tubing. The canister was then pressurised to 40 psi with nitrogen. Successive dilutions of the canister contents were used to reach lower concentrations.

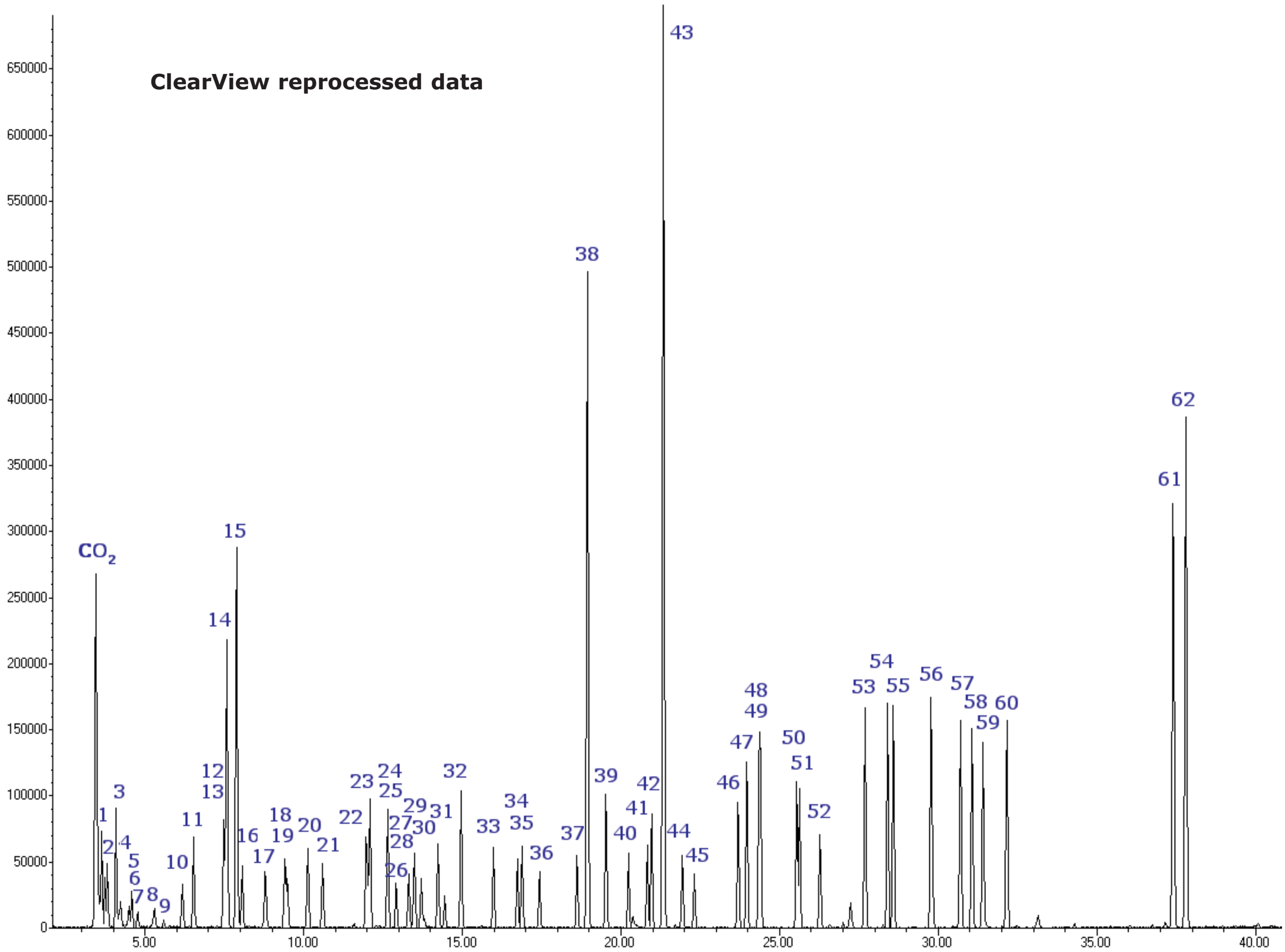

Figure 2: Splitless analysis of 1 L of a 1 ppb TO-15 standard using a column for purgeable volatiles (A). Note narrow Gaussian peak shapes

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)	*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 1: Elution order for the splitless analysis of 1 L, 1 ppb TO-15 standard on column A

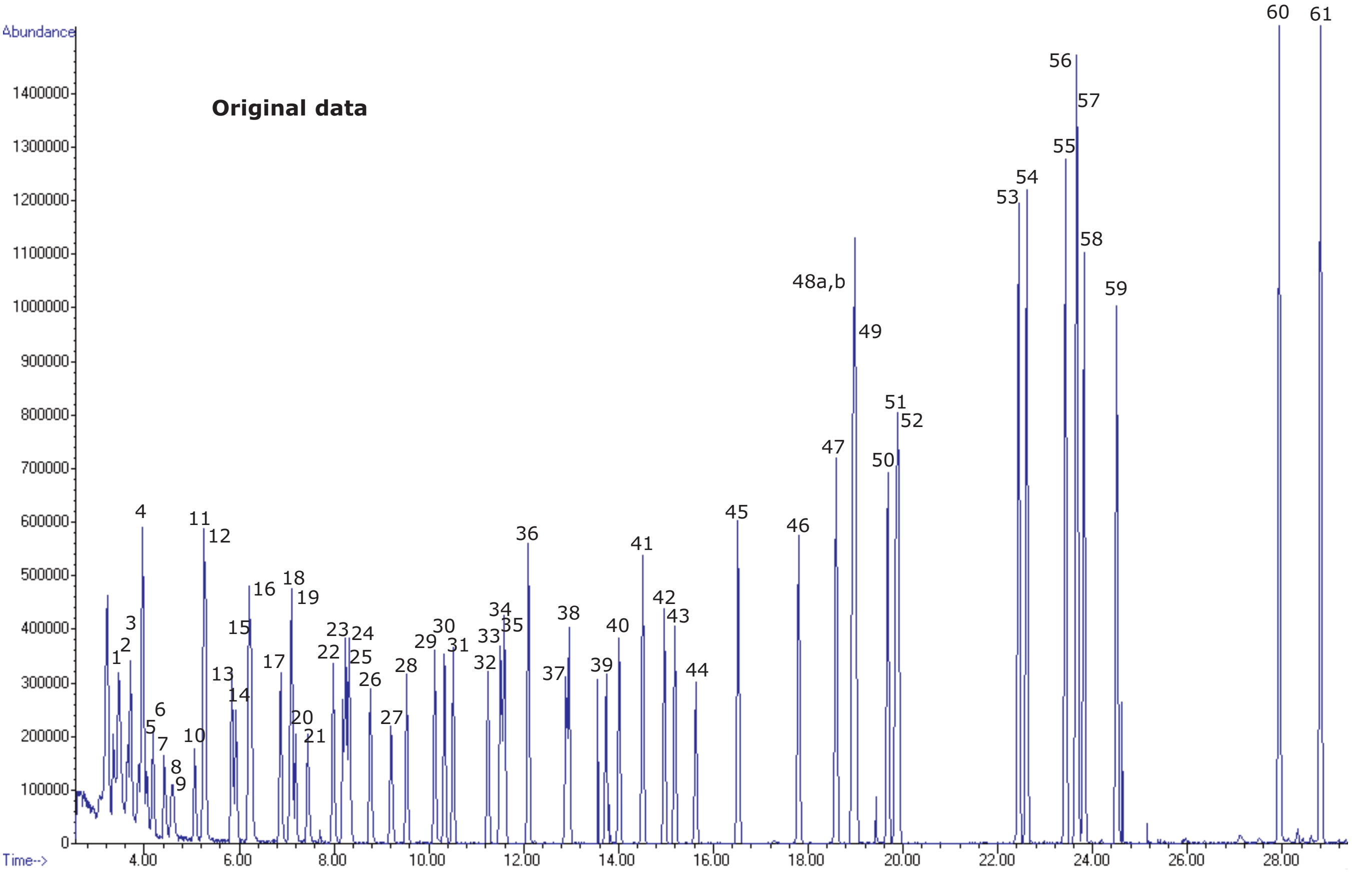

Figure 3: Split analysis of a 100 ml, 25 ppb TO-15 standard using a bonded methyl silicone column (B) and scan mode. Note narrow Gaussian peak shapes

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

Table 2: Elution order for the split analysis of 100 ml, 25 ppb TO-15 standard using column B

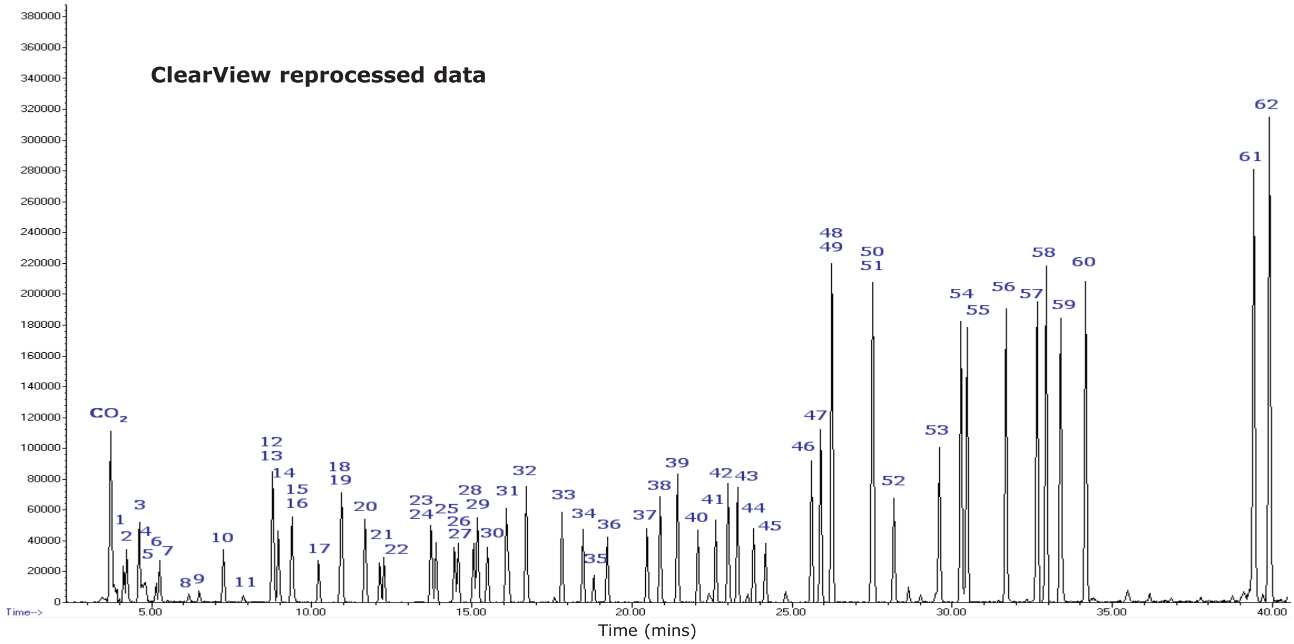

Figure 4: 1 L of a 1 ppb TO-15 standard analysed splitless using a column for purgeable volatiles (C). Note narrow Gaussian peak shapes

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) 49) 50)	*o*-, *m*-, *p*-Xylene + ethylbenzene
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 3: Elution order for the 1 ppb standard analysed using column C

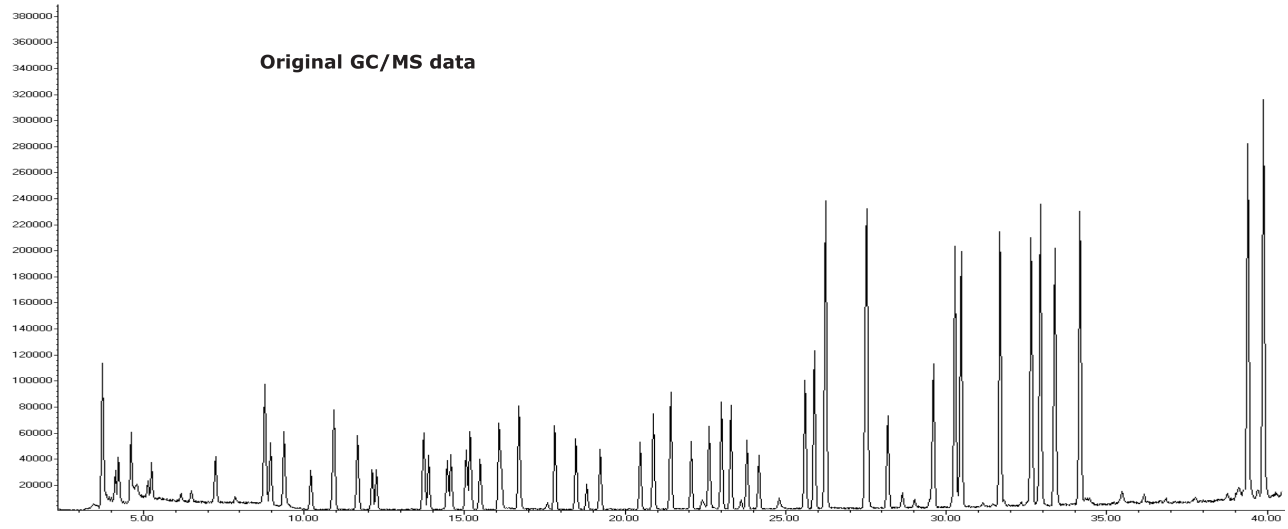

Figure 5: 1 L of a 1 ppb air toxics standard as shown in figure 4, but without ClearView. Note minor baseline anomaly due to residual water early in the run

Results

Figures 2 - 45 show air toxics analyses carried out using the series 2 UNITY-CIA 8 system under 3 different sets of GC/MS analytical conditions.

Trap desorption efficiency is illustrated by the excllent peak shape of early eluting components, including polar species such as isopropanol (IPA). See also in close-up in figures 6 and 7.

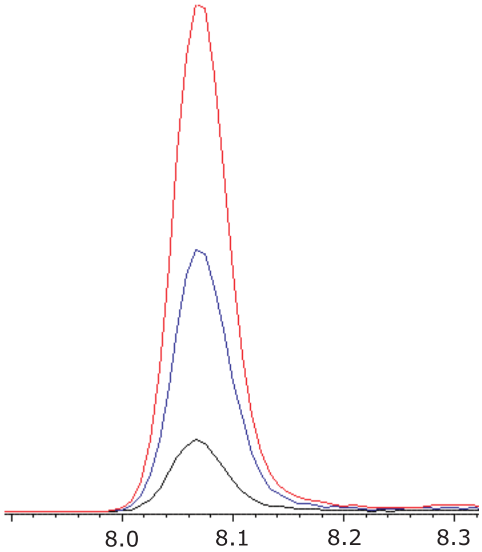

Figure 6: Peak shape for IPA at 0.6 ppb (red), 0.3 ppb (blue) and 0.1 ppb (black) analysed splitless using extracted mass ion 45 and column A

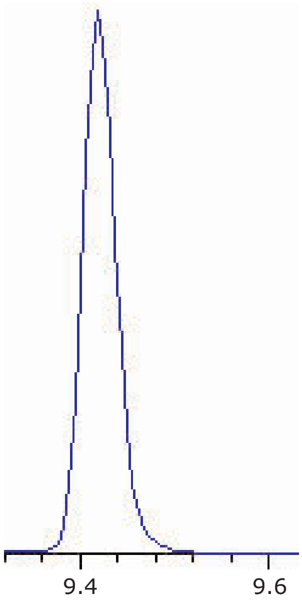

Figure 7: Peak shape for 1 ppb IPA analysed splitless, using extracted mass ion 45 and column C

Note that the excellent peak shape and level of sensitivity achieved in each case was obtained without the use of liquid cryogen, either for analyte trapping or for refocusing components on the front of the GC column.

GC/MS data from the air toxics analysis carried out using columna A and C are shown in figures 2 and 4 with the benefit of ClearView reprocessing. 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 5.

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 8).

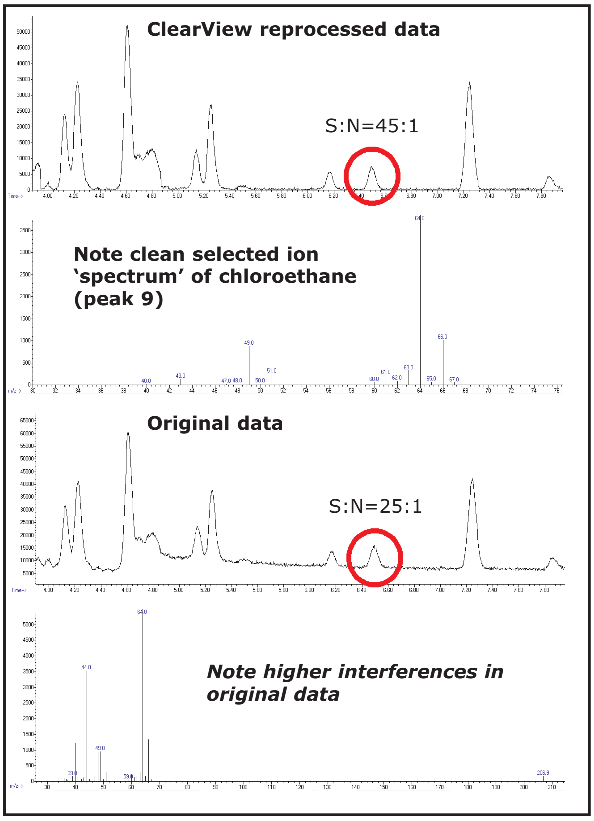

Figure 8: Expanded portions of the air toxics standard analysis (figures 4 & 5) showing ClearView enhancement of spectral purity and signal:noise

Minimum detection limits were well below 0.1 ppb for all compounds, under all conditions tested (split, splitless and full scan)
[*N.B.* Assumes extracted ion and 1 L air sample volumes].
Measurement at lower levels could be readily achieved by using the MS in Selected Ion Monitoring (SIM) mode.

The system performance data, shown below (linearity, IS precision and system reproducibility), were obtained using column C but are typical of results obtained under all 3 sets of conditions.

Linearity

Figure 9 illustrates system linearity with R^2 values of 0.99, 0.99, 0.99 and 0.98 for benzene, bromodichloromethane, dibromochloromethane and bromomethane respectively.

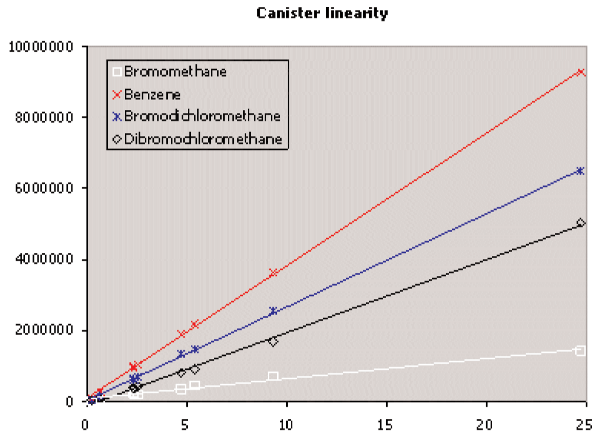

Figure 9: Linearity plots from 0.1 to 25 ppb

Internal standard addition

Series 2 UNITY-CIA 8 TD systems feature the capability to introduce 1 ml gas-phase internal standard (IS) to the focusing trap of UNITY 2 during sample introduction in compliance with Method TO-15. IS addition enhances the precision of sample and external gas standard analysis.

To test this capability, the IS addition module of CIA 8 was used to make four repeat injections of a ppm level gas-phase standard of benzene, toluene and xylene. The results can be seen in table 4.

Analyte	Mean Peak Area (n=4)	% RSD
Benzene	13967	0.85
Toluene	18715	0.81
Xylene	22507	0.77

Table 4: Reproducibility data for internal standards

System reproducibility

Well documented issues relating to sample stability in low pressure canisters[1] make them unsuitable for system stability tests. The repeatability of the series 2 UNITY-CIA 8 air toxic analyzer was therefore evaluated by introducing 1 ml aliquots of 1 ppm level TO-15 standard to the UNITY 2 focusing trap in a stream of pure nitrogen (*N.B.* 1 ml of 1 ppm standard is equivalent to a 1 L volume of 1 ppb standard.)

Five repeat analyses were carried out and % RSDs for 8 example compounds, covering the volatility and polarity range of the TO-15 standard, are shown in Table 5. **Results range from 1.9 – 4.5% RSD.**

Compound	% RSD
Dichlorodifluoromethane	2.8
IPA	4.0
Carbon disulphide	2.8
Dichloroethylene	3.3
THF	2.2
Benzene	1.9
Vinyl chloride	4.0
1,2,4-Trichlorobenzene	4.5

Table 5: System reproducibility demonstrated using 8 compounds covering a typical range of 'air toxic' volatilities and polarities

Conclusions

These results illustrate the excellent chromatographic performance of the Markes Series 2 UNITY-CIA 8 system for TO-15 air toxics, operating **cryogen free** and under three sets of analytical conditions. Quantitative detection of TO-15 air toxics ranging from methyl chloride to hexachloro-1,3-butadiene has also been demonstrated at levels down to 0.1 ppb in canisters. Even lower levels could be comfortably achieved by using the MS in SIM mode.

The ability of the CIA 8 to introduce reproducible aliquots of gas-phase internal standard has been demonstrated. This capability will improve the precision of external air toxics standards in compliance with the requirements of TO-15.

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.