NEMC

Analysis of TO-15/TO-17 air toxics in urban air using TD–GC/TOF MS and automated compound identification software

NEMC, Washington D.C. August 6th 2012

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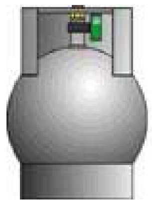
Thermal desorption – One versatile technique for all vapour-phase air monitoring applications

Electrically-cooled focusing trap

Online

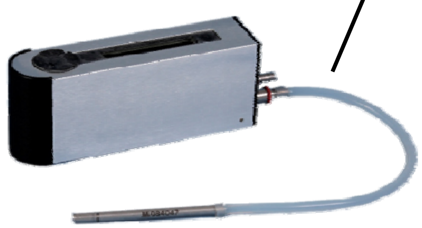
Canisters/bags

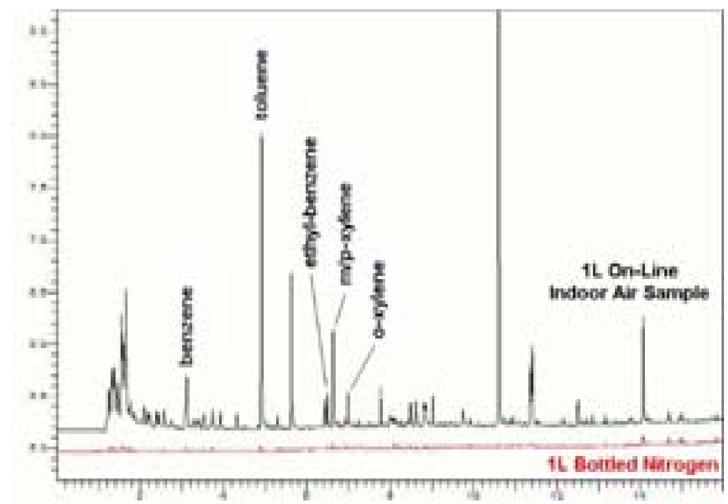


Sorbent tubes

Passive

Active





Injection of 100–200 µL vapour into GC(MS)

Water and volatile interferences can be purged to vent

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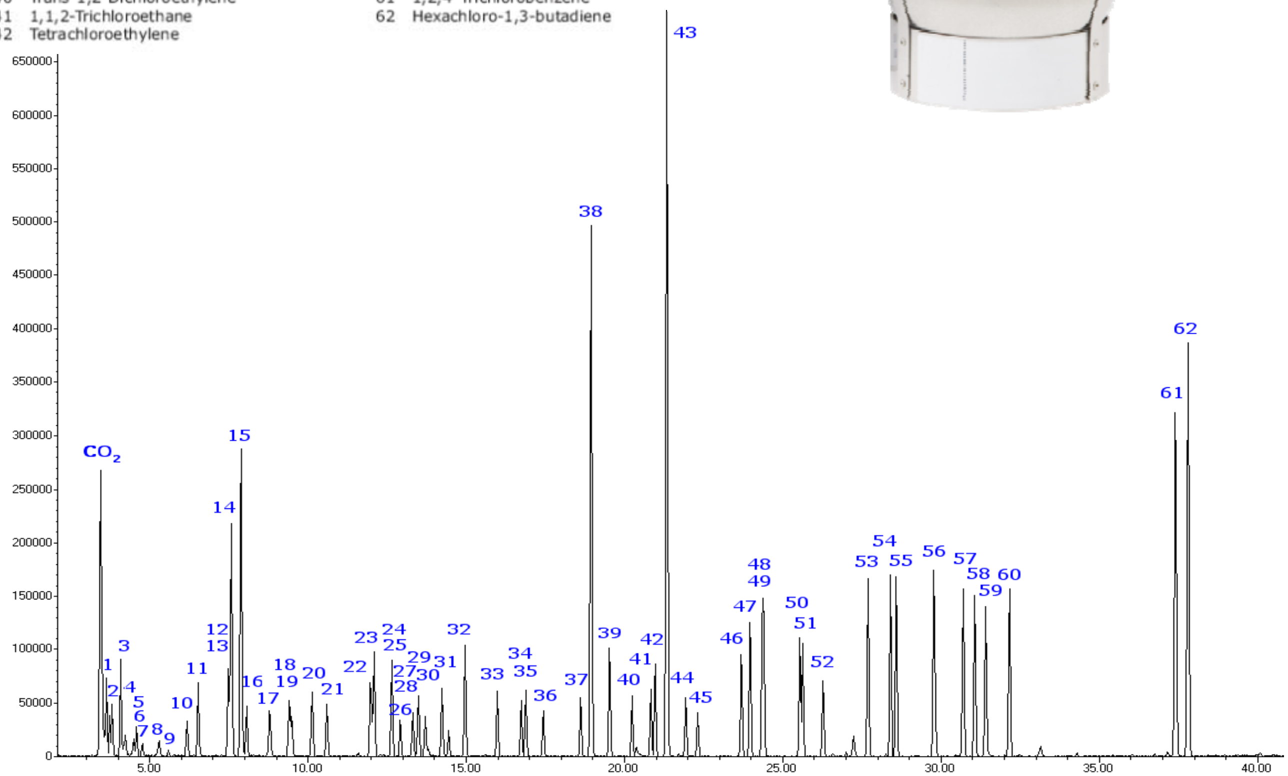
Application: 'Air toxics' in canisters – US EPA Method TO-15

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

1 L of a 1 ppb air toxics mix analysed splitless and cryogen-free using TD–GC/MS scan



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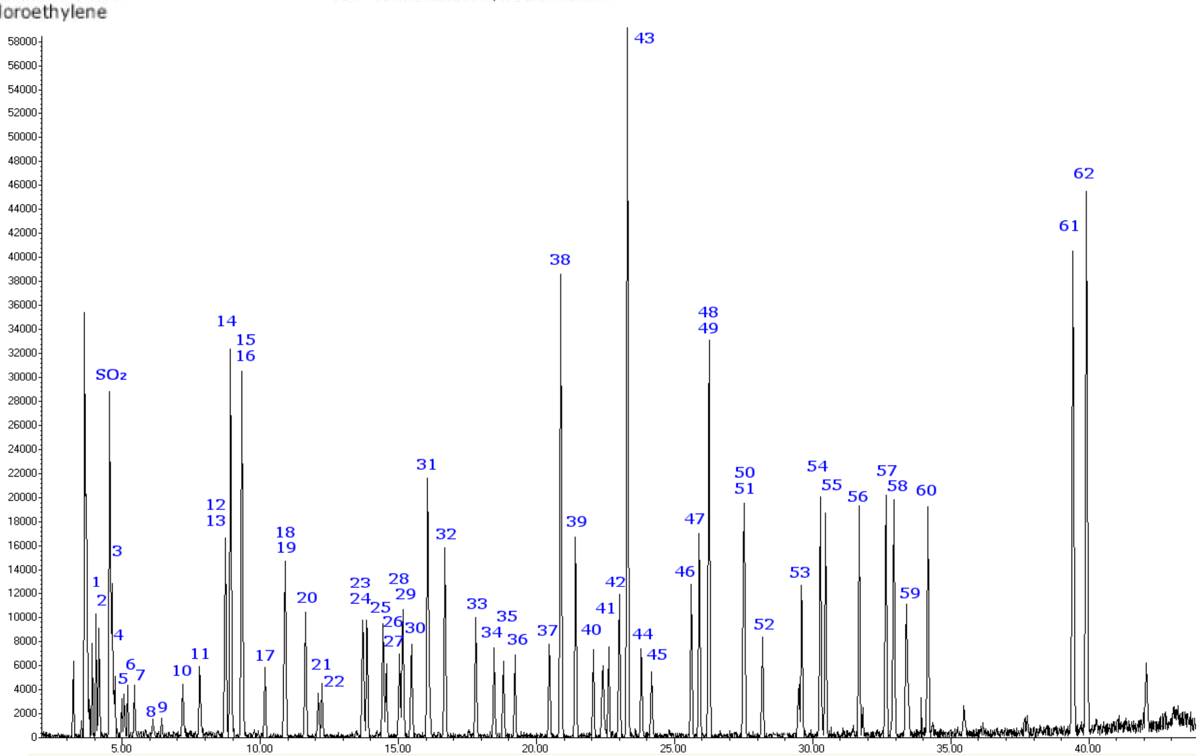
Application: 'Air toxics' using sorbent tubes – US EPA Method TO-17

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

Splitless desorption of 'Air toxics' tube loaded with 1 L of 1 ppb std GC/MS



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Can canisters do everything?

- ✓ Great for C_2 to C_{12} compounds
- ✓ Suitable for rapid transfer (not storage) of ultra-volatile reactive compounds such as H_2S
- ✓ Ideal for simple grab-sampling

- x NOT suitable for compounds with volatility less than $C_{10/12}$
- x NOT suitable for high-concentration samples
- x Time-weighted average sampling is NOT easy with a canister

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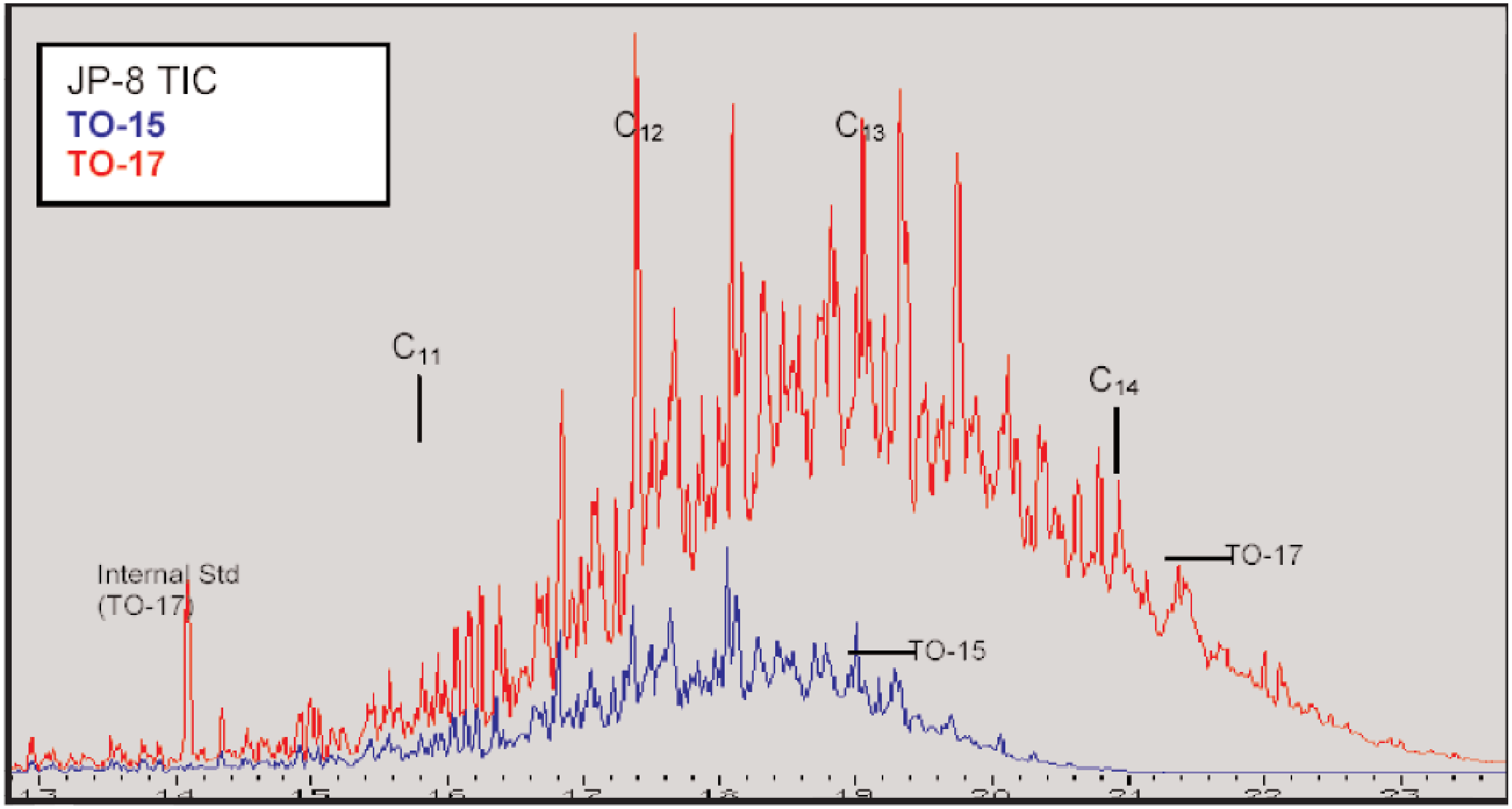
Application: Soil gas



Profiles of soil gas contaminated with kerosene obtained using:

(a) Canister sampling and TO-15 analysis (blue)

(b) Sorbent tube sampling with TO-17 analysis (red)

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Courtesy of H. Hayes, Eurofins Air Toxics, Folsom

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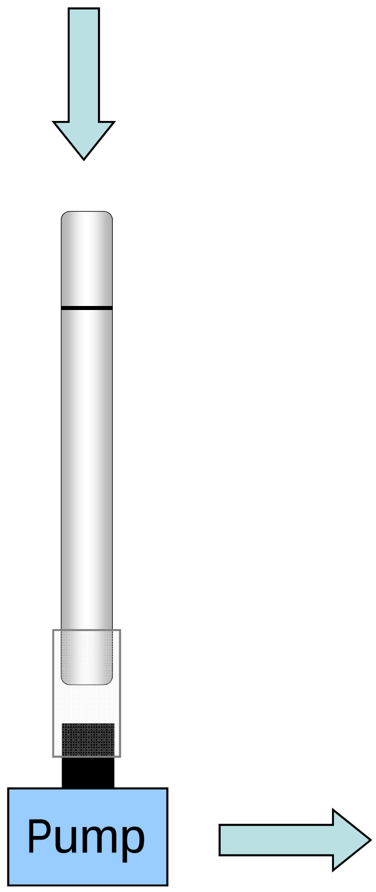
Active (pumped) sampling

- TO17 specifies “The monitoring procedure involves pulling a volume of air through a sorbent packing to collect VOCs”
- Flow rate typically 20 – 100 ml/min
- Volume taken is typically in the range 5 ml – 100 L, depending on expected concentration (typically two samples 1 L and 4 L)
- Much faster technique compared to diffusive sampling
- Important do not exceed breakthrough volume for a compound on a given sorbent



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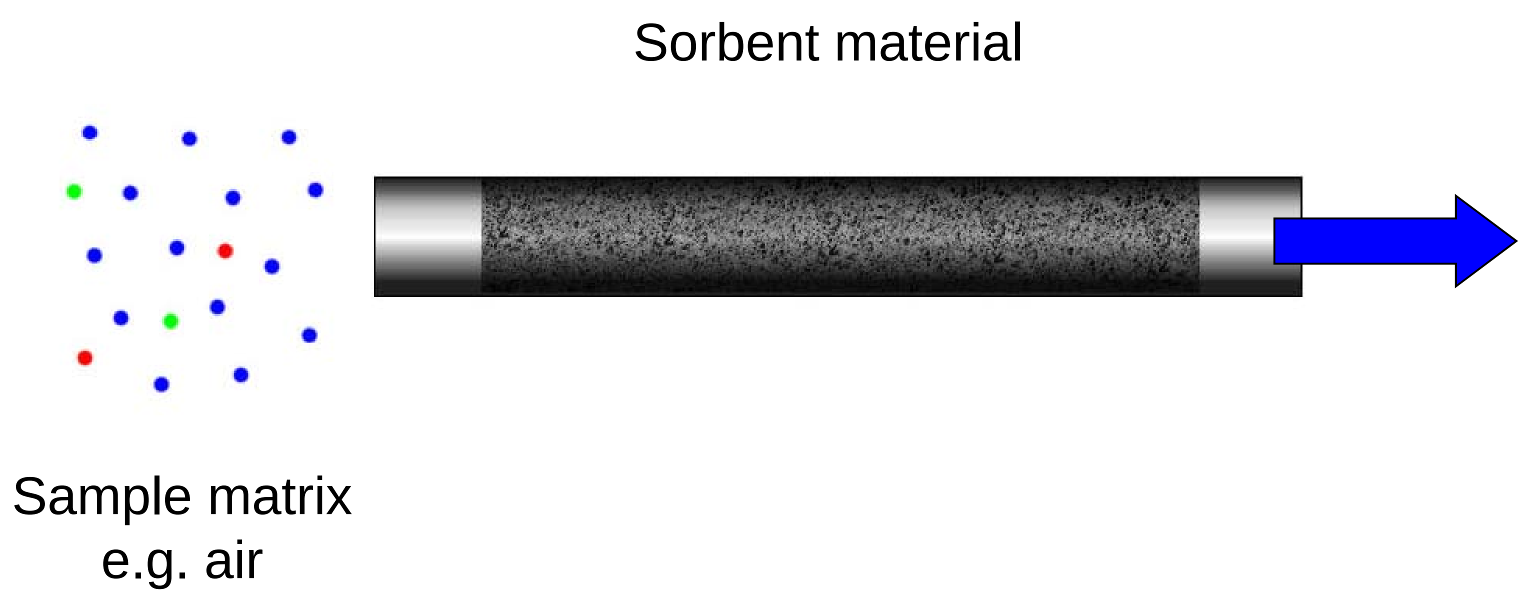
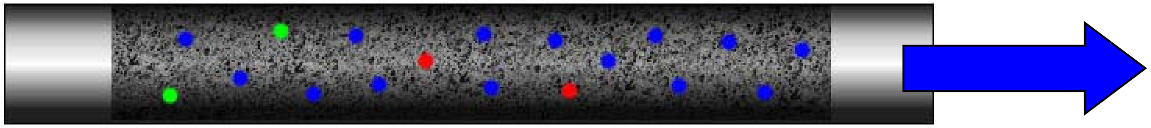
Tube-based thermal desorption – An overview of the process



Tube-based thermal desorption

Sample passes onto the sorbent



Compounds of interest are adsorbed on the sorbent surface

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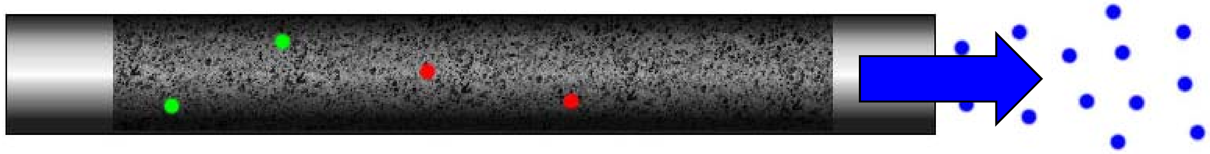
Tube-based thermal desorption



Lighter gases such as nitrogen pass through the sorbent

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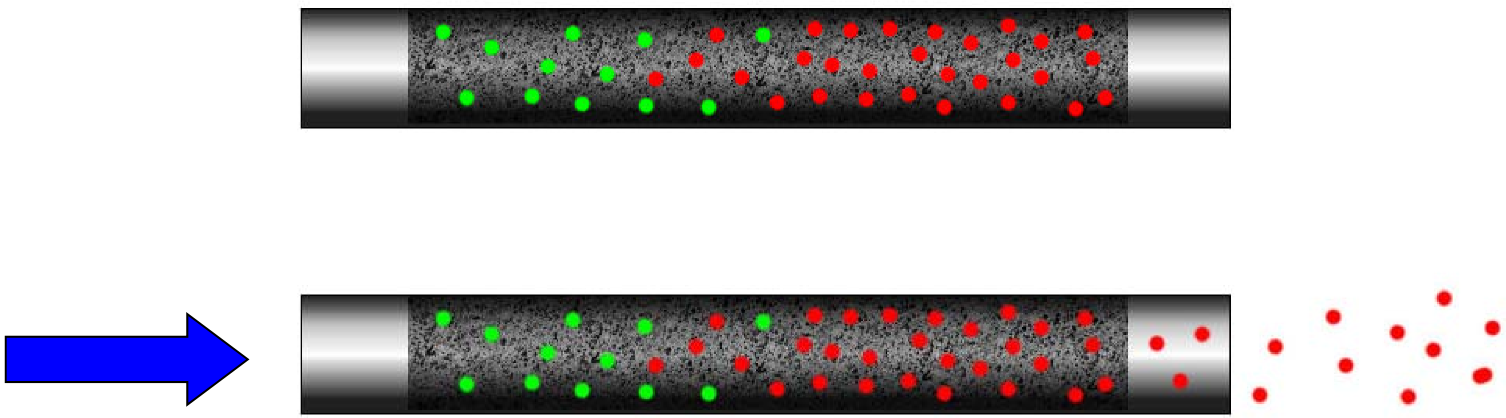
Breakthrough



Affected by:

Temperature	lower temp. = stronger interaction
Sample volume	lower volume = less risk of breakthrough
Mass or sorbent	more sorbent = more surface area
Type of sorbent	stronger sorbent = stronger interaction

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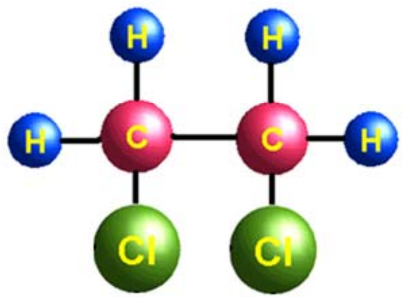
Air monitoring – Pumped

Sorbent selection for both tubes and focusing trap are very important

Semi-volatile compounds – Weak sorbent
Helps prevent retention of unwanted compounds

Very volatile compounds – Strong sorbent
Prevents breakthrough of light compounds



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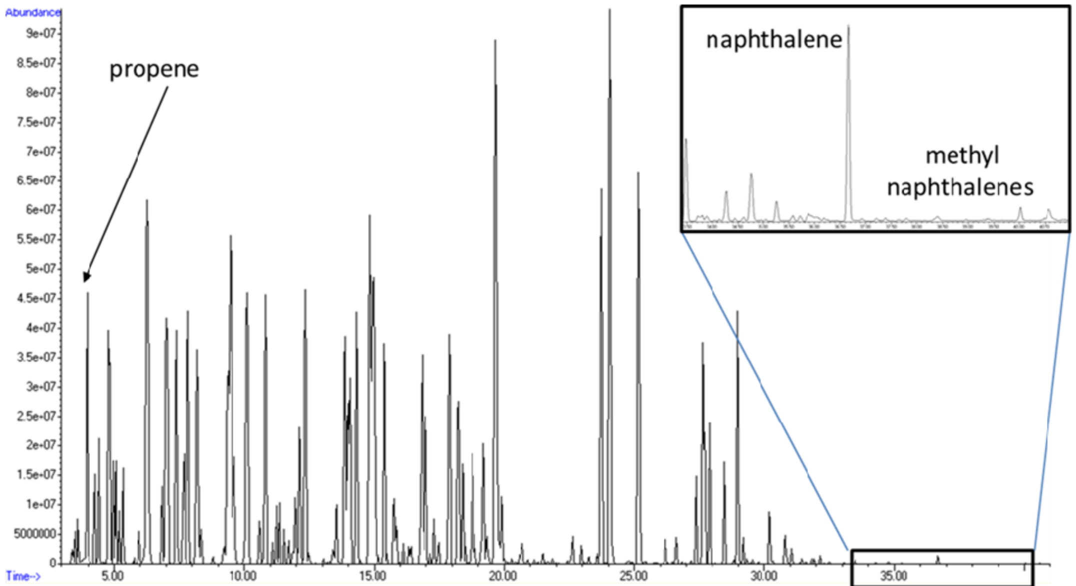
Common sorbents

Sorbent name	Volatility range
Quartz wool / silica beads	$C_{30} – C_{40}$
Tenax TA	$C_7 – C_{30}$
Carbograph 2TD	$C_8 – C_{20}$
Carbograph 1TD	$C_{5/6} – C_{14}$
Carbograph 5TD	$C_{3/4} – C_{6/7}$
SulfiCarb	$C_3 – C_8$
Carboxen 1003	$C_2 – C_5$
Carbosieve SIII	$C_2 – C_5$

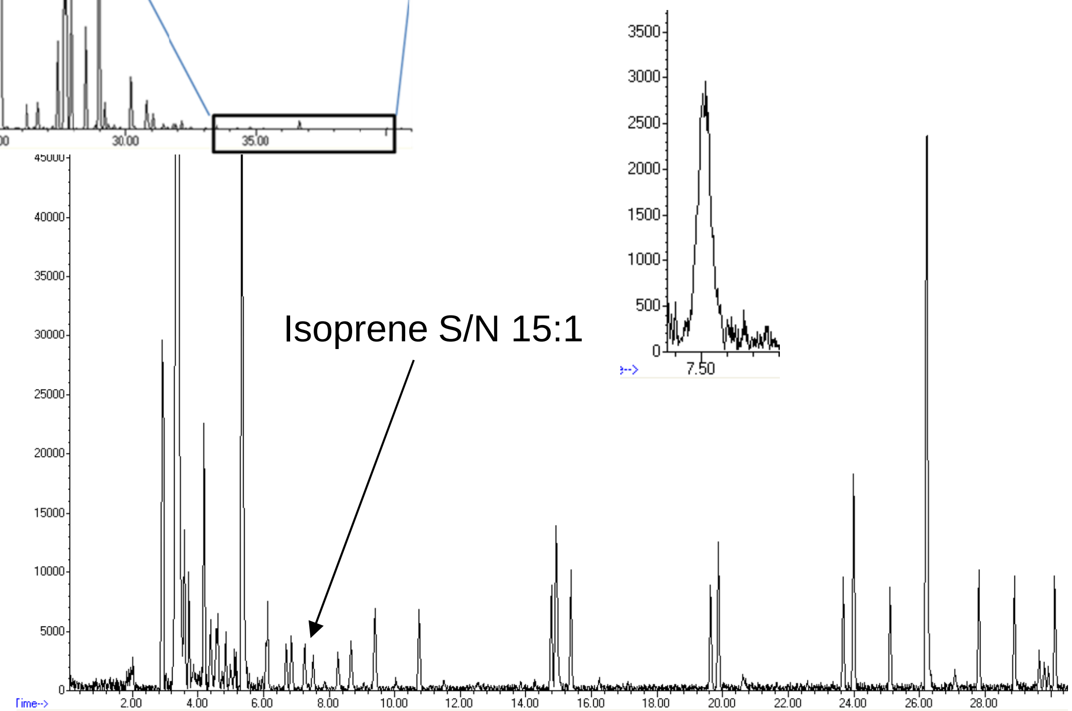
Water retention

Application examples – High/Low concentration



50 mL sample of
diesel exhaust

500 mL sample of
4 ppb ozone
precursor standard



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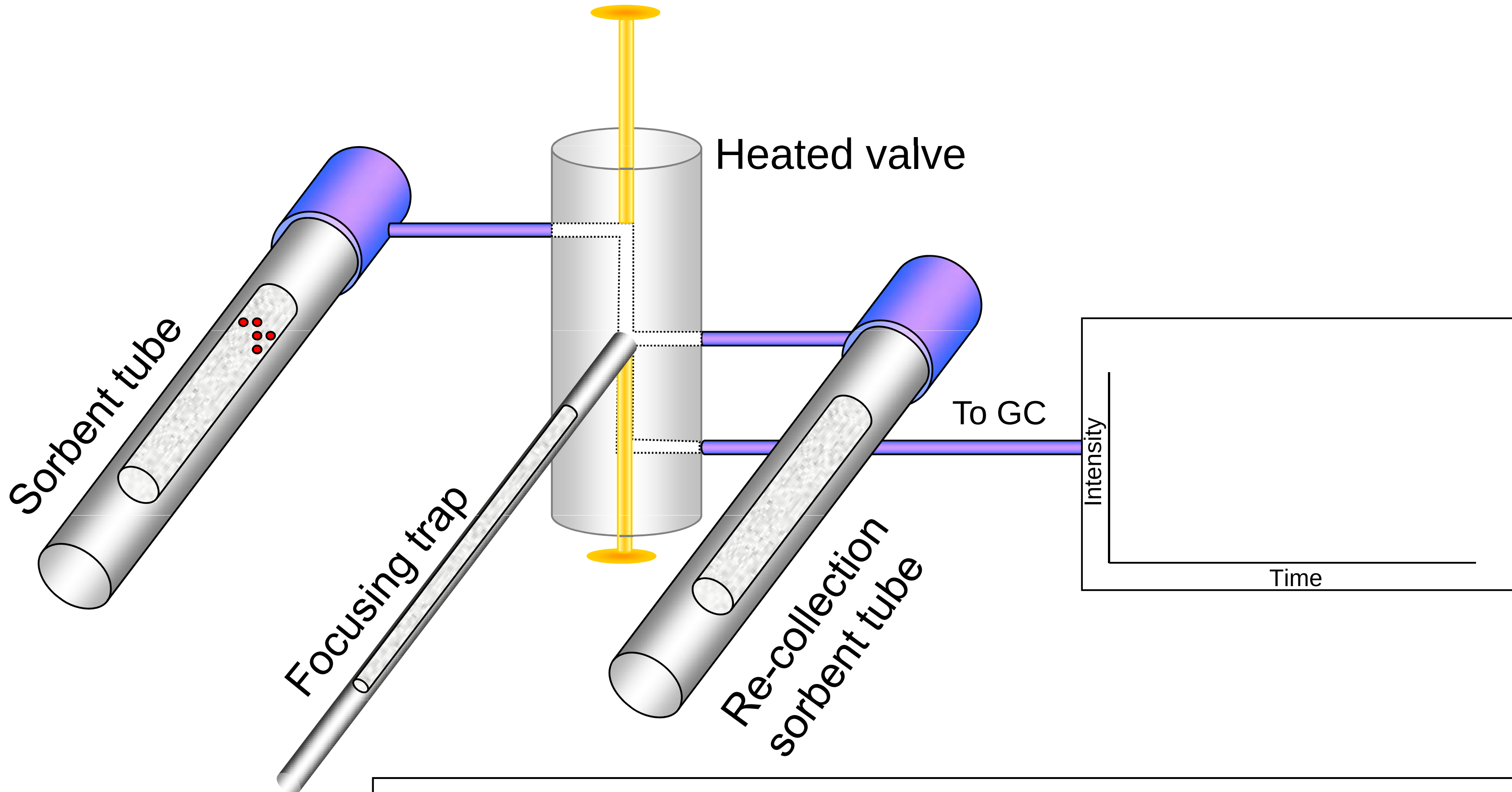
Sample security using sample re-collection

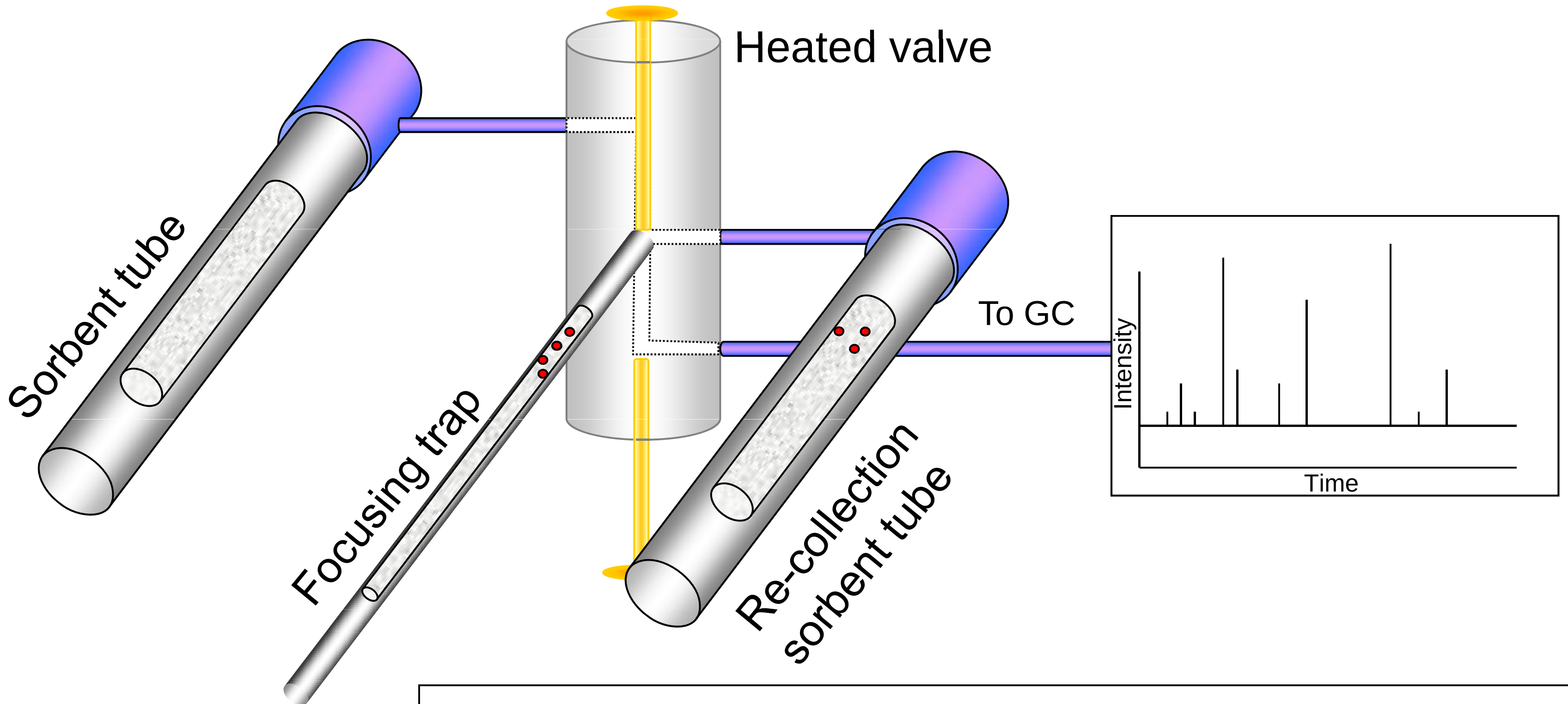
Stage 1: Primary (tube) desorption with optional (inlet) split



- Patented heated valve is inert and low volume: Allows quantitative recovery of high and low volatility and reactive compounds
- The heated valve isolates the TD system allowing method compliance: leak testing, backflush trap desorption, purge to vent, overlap mode, *etc.*

Sample security using sample re-collection

Stage 2: Secondary (trap) desorption with optional (outlet) split



- Repeat analysis of re-collected samples makes it easy to validate analyte recovery through the TD flow path
- A change to the overall VOC profile indicates any bias

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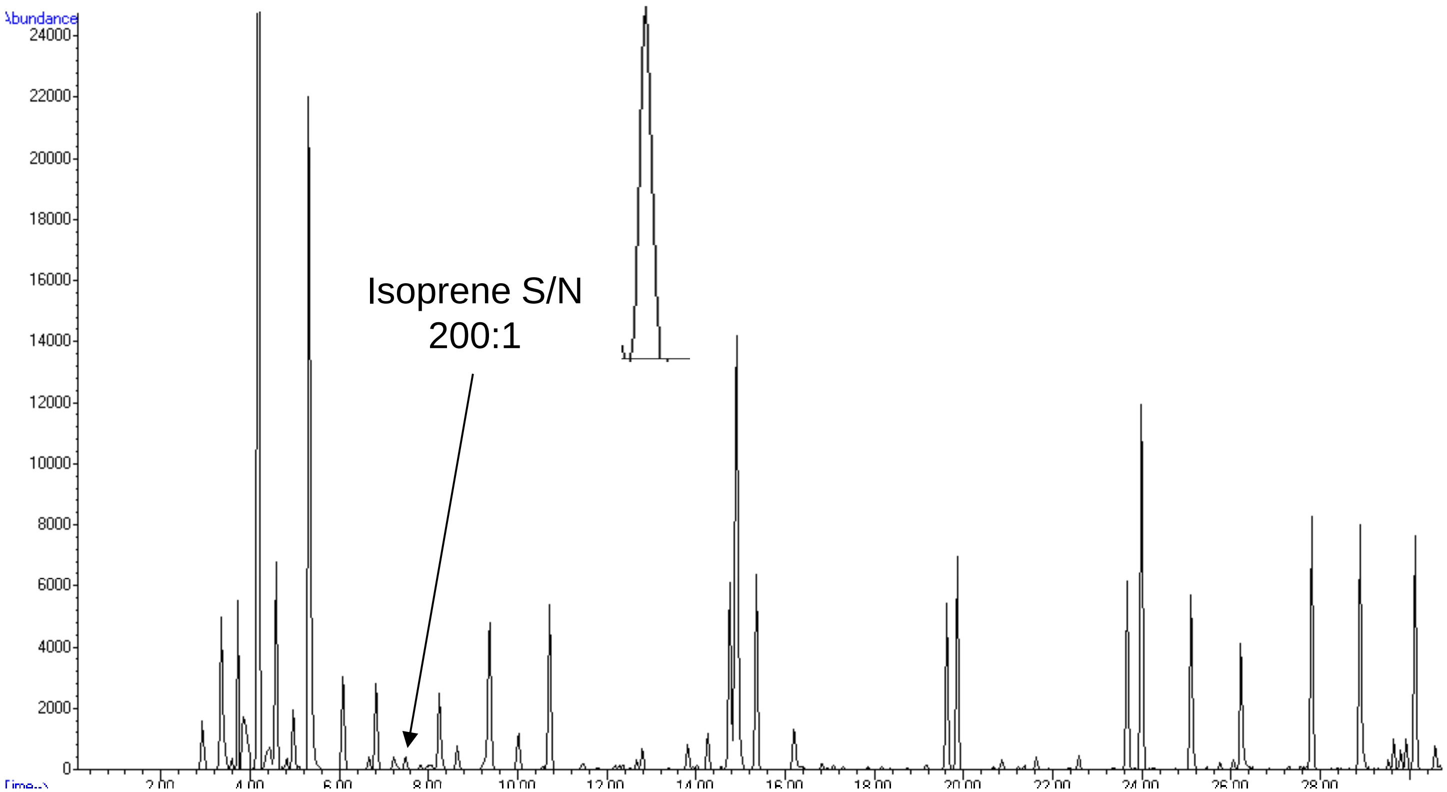
Re-analysis of low-concentration sample

The 4 ppb standard was re-collected for re-analysis using SIM detection conditions



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BenchTOF-dx:
Detector enhancements for air monitoring

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ALMSCO international

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What does BenchTOF-dx offer?

- **S**pectral accuracy cannot be compromised
- **S**ensitivity is **KING**
- **S**peed can be leveraged for deconvolution
- **S**electivity – enhanced mass resolution should mainly be used to limit the matrix in VOC work (high res has limited advantages)
- **S**tability is key to productivity

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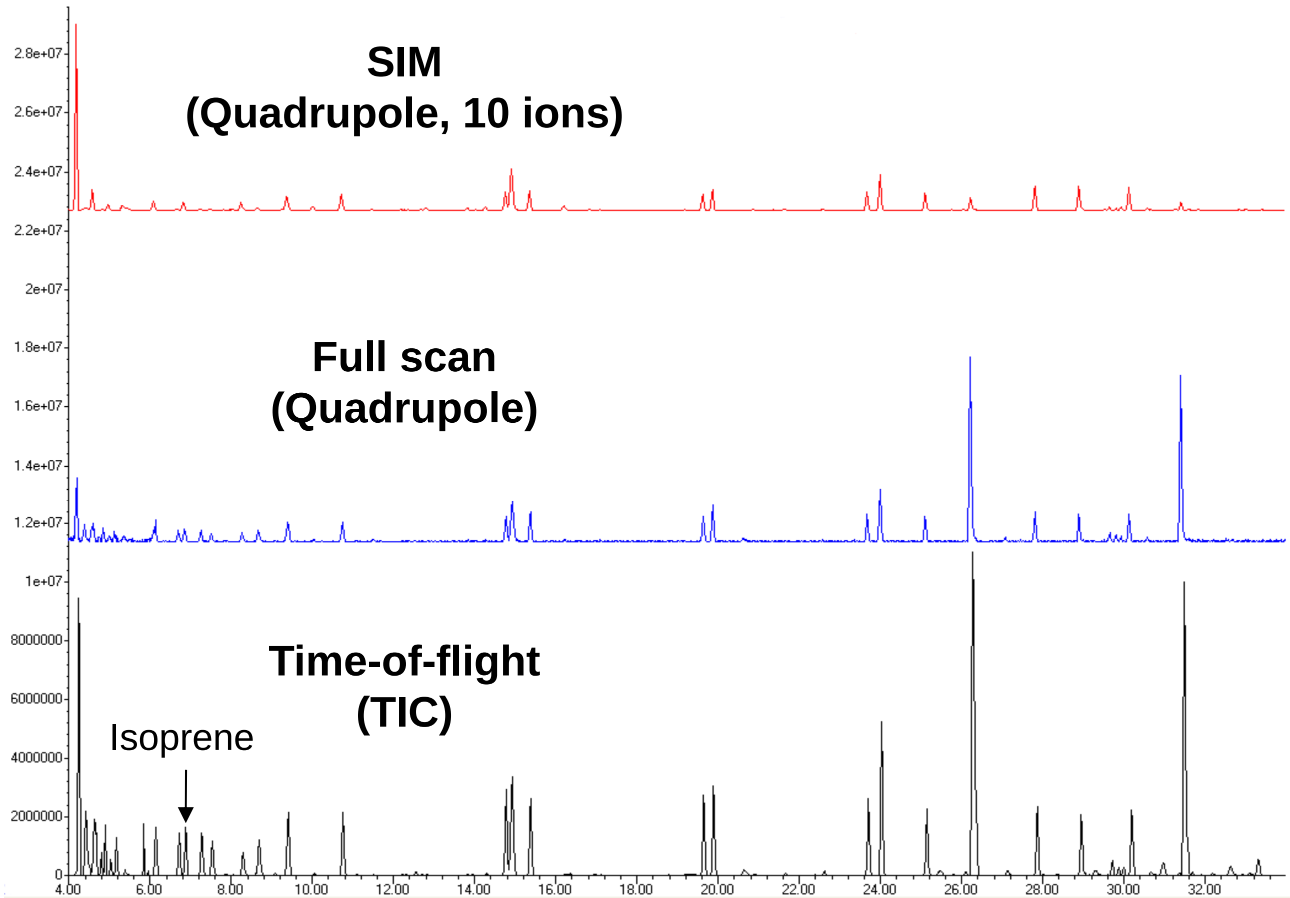
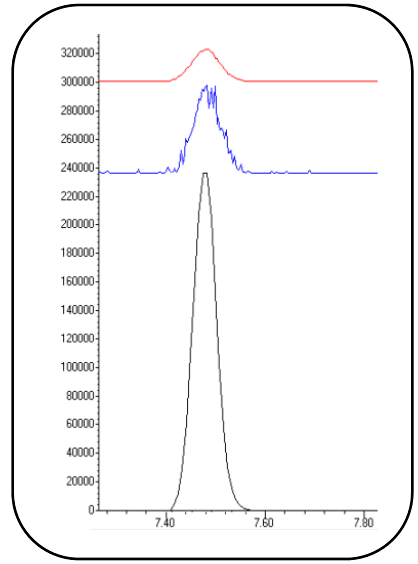
Quadrupole comparison

500 mL sample of 4 ppb ozone precursor standard





Detection method	S/N
Full scan (Quad)	15:1
SIM (Quad)	200:1
BenchTOF-dx	1500:1

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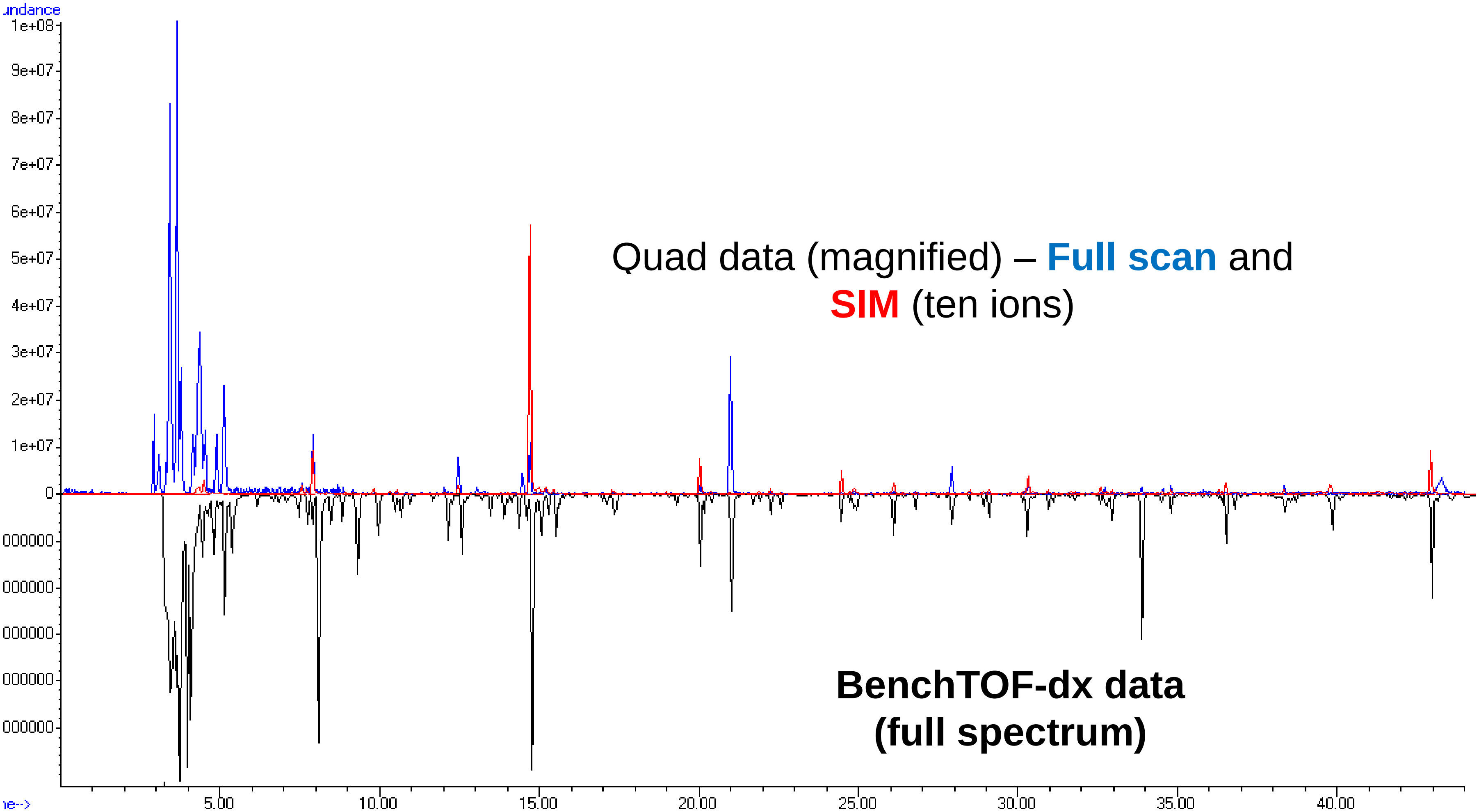
Quadrupole comparison

200 mL sample of ambient rural air



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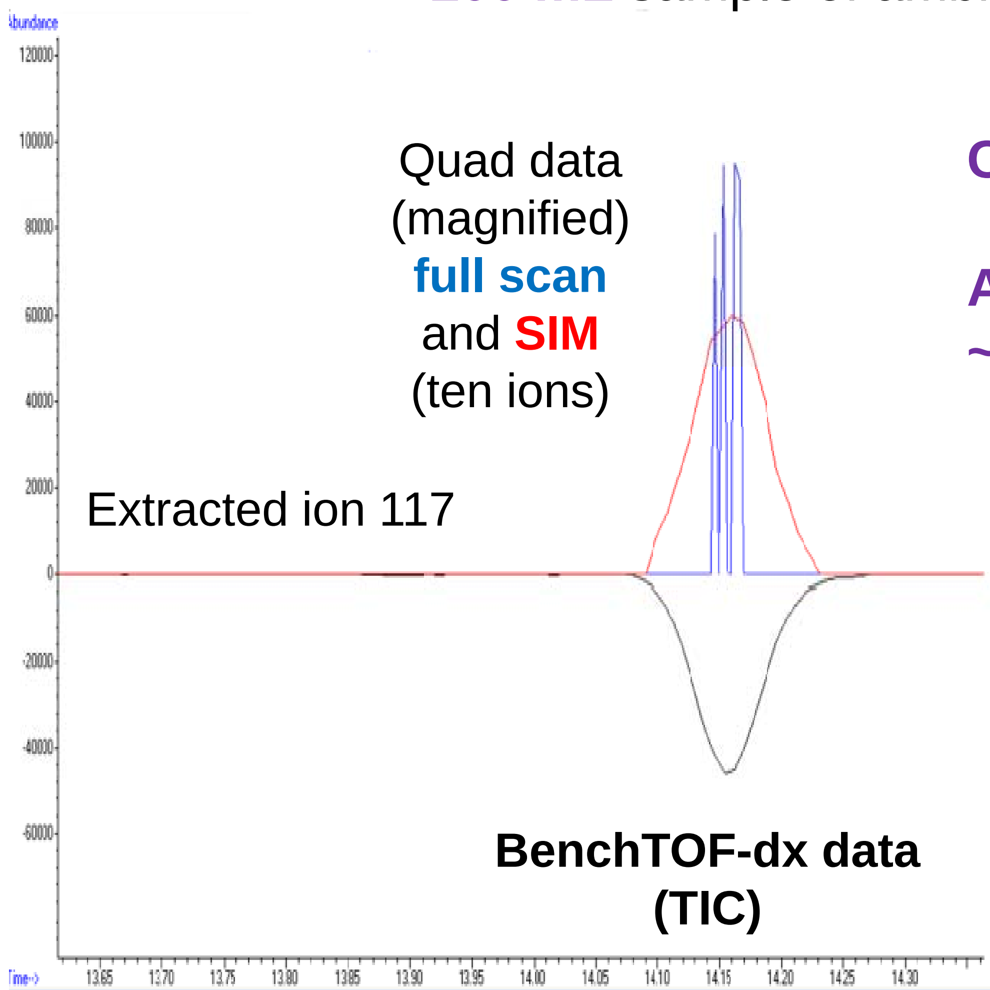
Quadrupole comparison

200 mL sample of ambient rural air



Carbon tetrachloride

Atmospheric concentration ~100 ppt (~ 85 pg on column)

Detection method	S / N
Full scan (Quad)	ND
SIM (Quad)	100:1
BenchTOF-dx	700:1

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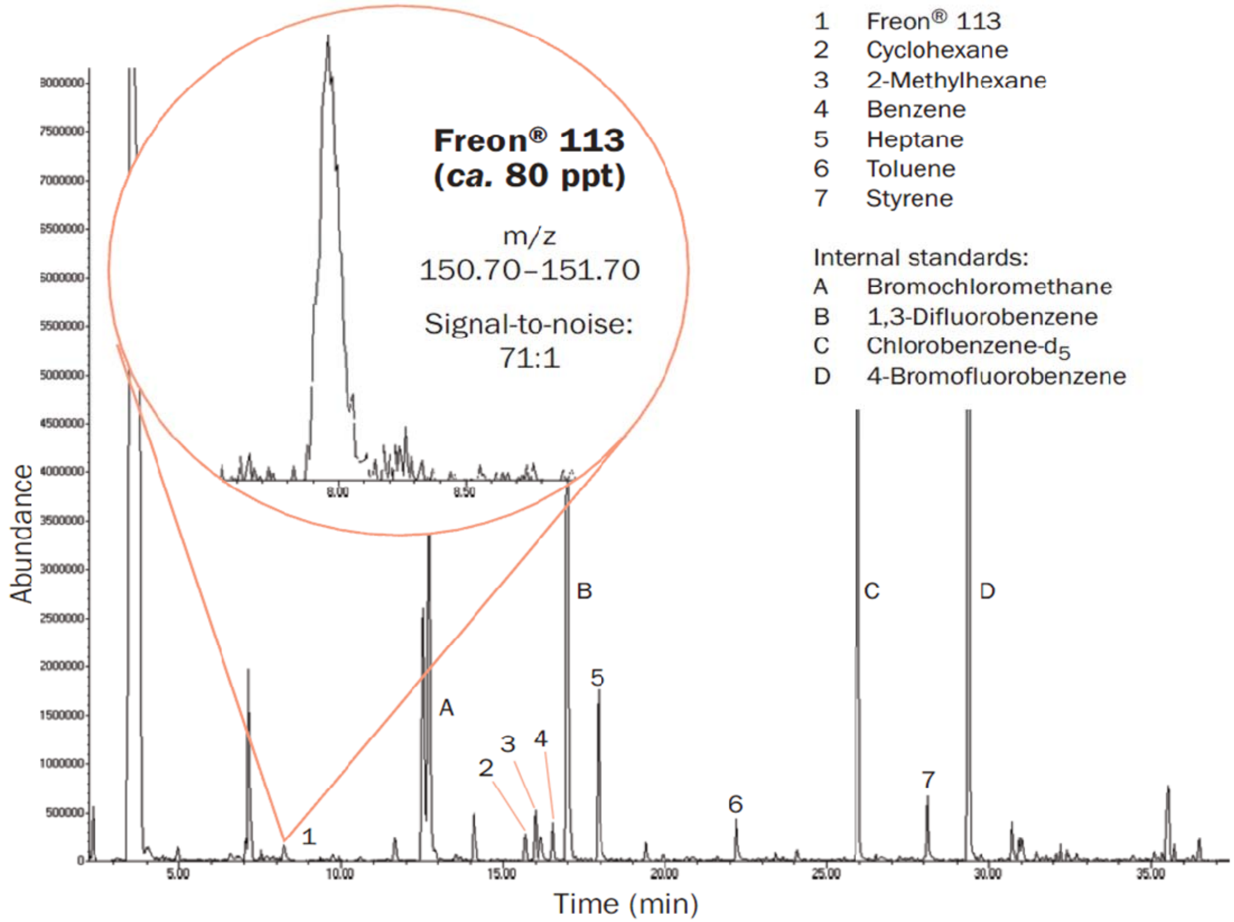
10 mL of ambient semi-rural air



Total ion chromatogram showing splitless analysis of only **10 mL** of semi-rural air using TD–GC–TOF MS.

Inset: Extracted-ion chromatogram for a characteristic fragment ion of Freon® 113 (present in the atmosphere at *ca.* 80 ppt).

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How can I use a large sensitivity boost in air monitoring applications?

- Trace-level work for unknowns and targets combined at lower MDLs
- Smaller sample sizes but same MDLs
- Higher splits, cleaner system but same MDLs
- However you want to!

An investment in BenchTOF-dx provides a sensitivity boost!

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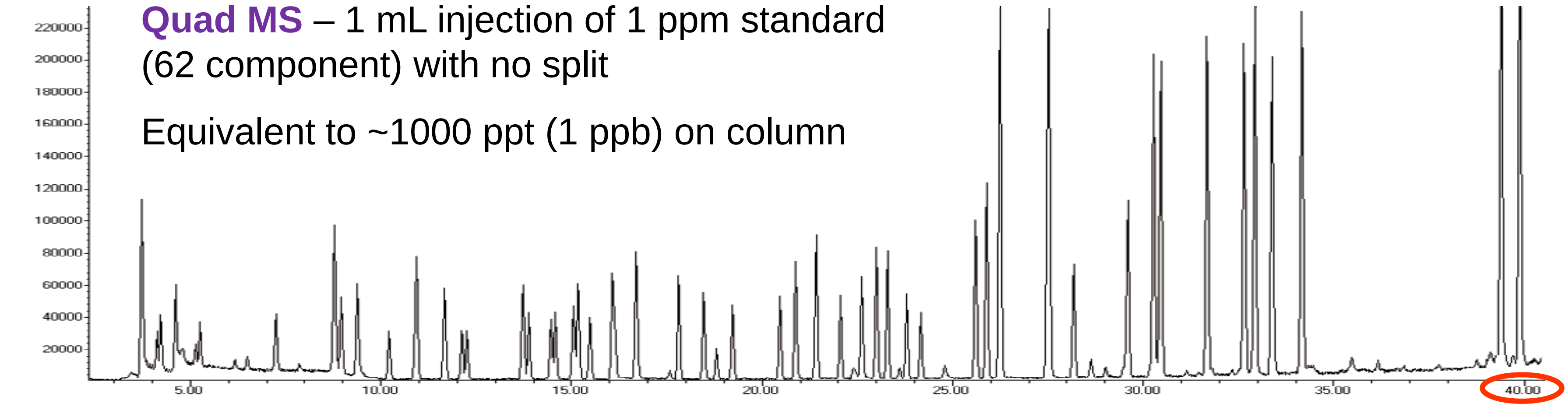
Provides productivity too!

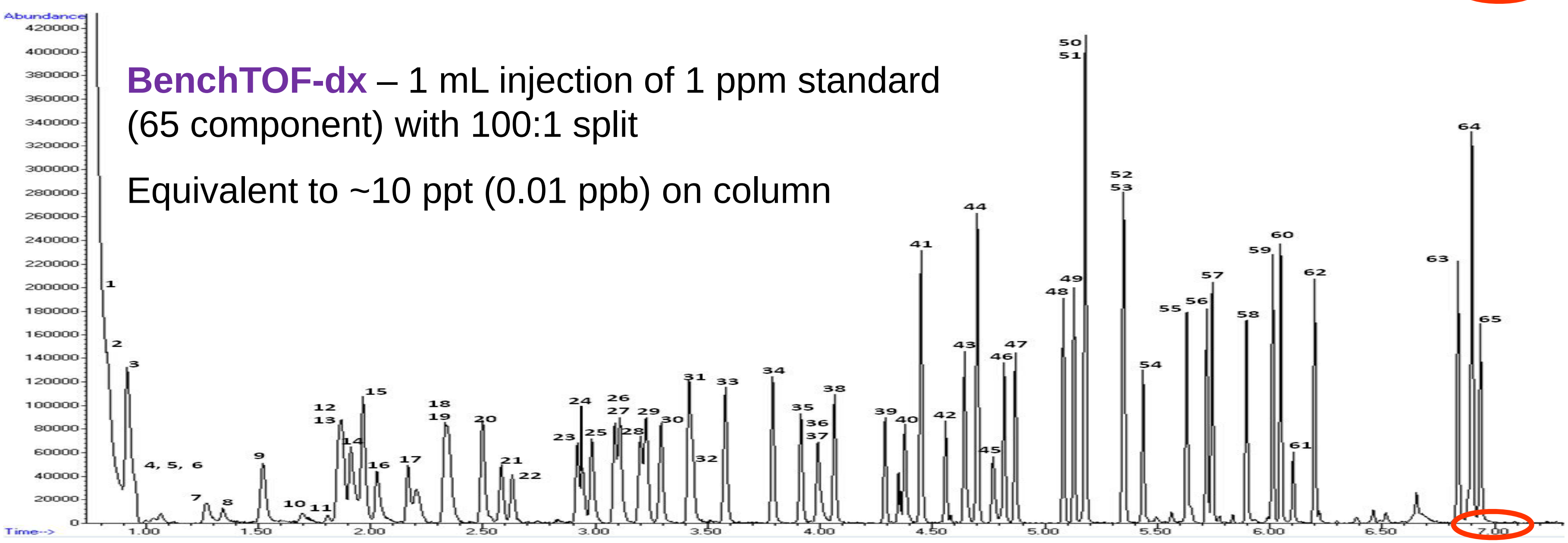
Quad MS – 1 mL injection of 1 ppm standard (62 component) with no split

Equivalent to ~1000 ppt (1 ppb) on column



BenchTOF-dx – 1 mL injection of 1 ppm standard (65 component) with 100:1 split

Equivalent to ~10 ppt (0.01 ppb) on column



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From 40 minutes to 7 minutes (4 runs in the time to do 1!)

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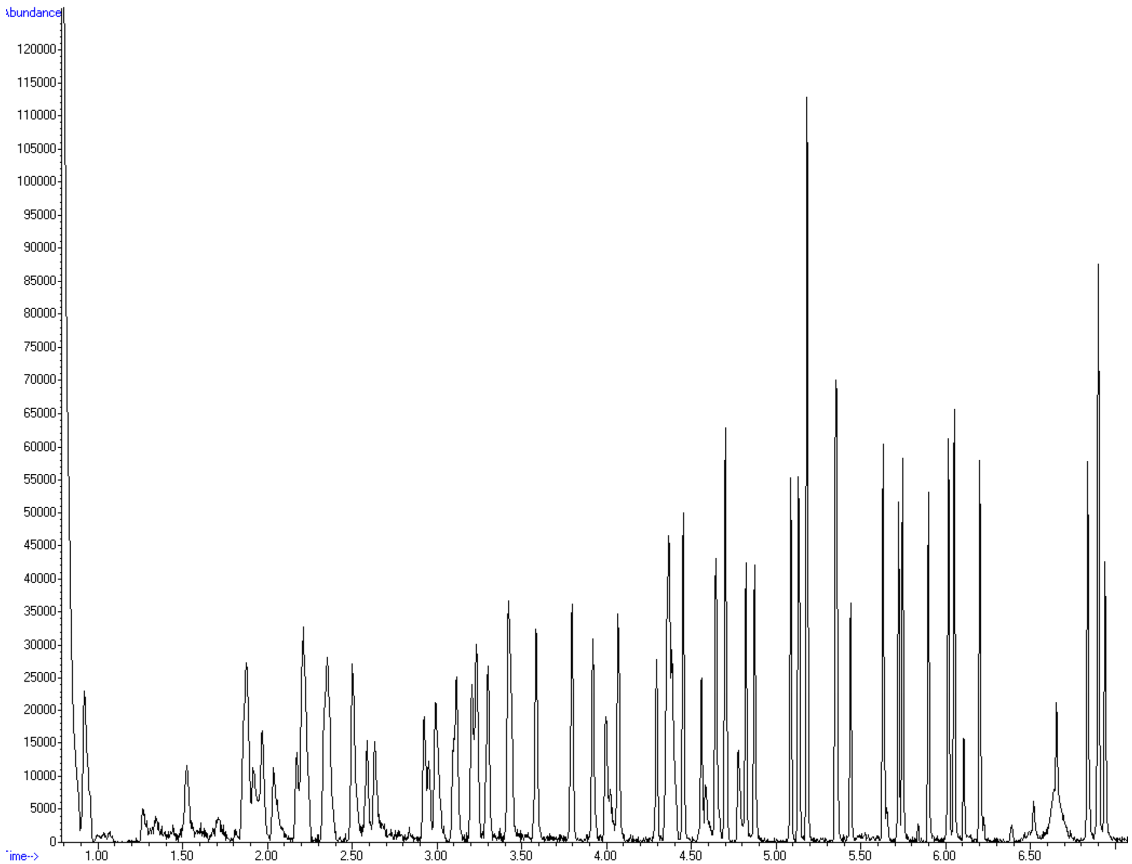
...without compromising sensitivity

BenchTOF-dx – 1 mL injection of 1 ppm standard (65 component) with 292:1 split

Equivalent to ~3 ppt (0.003 ppb) on-column



RMS signal-to-noise ranges from **15:1 to 1350:1** (non DBC)

LODs (assuming 3:1 minimum S/N) **0.01 ppt (10 ppq) to 0.6 ppt (600 ppq)**

BenchTOF-dx – at least 100 times better S/N than a quadrupole in full scan mode

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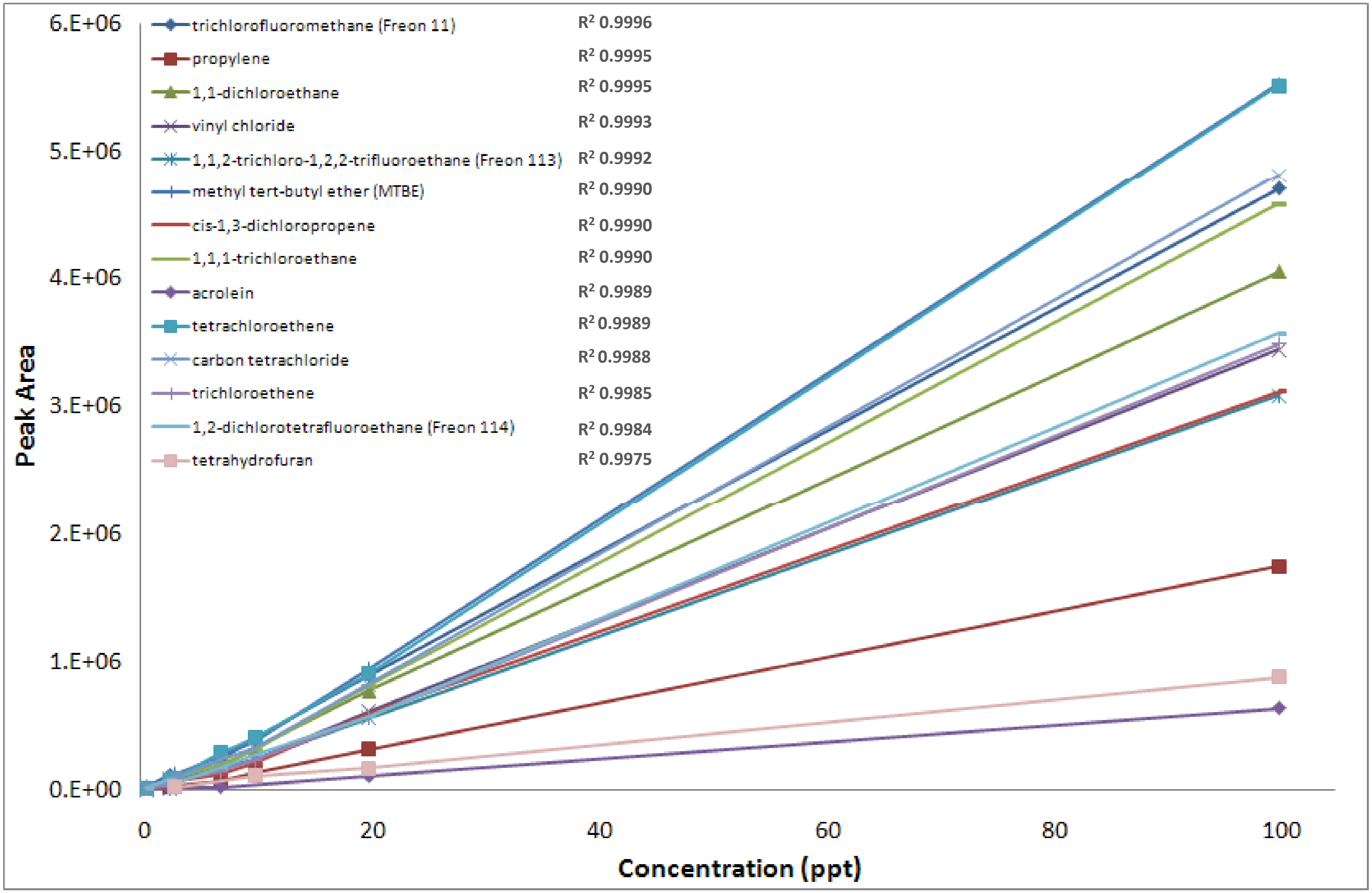
...whilst maintaining linearity



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Challenges associated with identifying target compounds in complex GCMS profiles

The problem…

- Identifying the presence of known toxic chemicals in complex GCMS TIC profiles is very challenging
- Technical capacity to interpret spectra is declining or absent, majority of analysts rely on commercial libraries (NIST, Wiley etc)
- Identification is complicated by chromatographic coelution of compounds and matrix effects, producing mixed spectra
- Conventional library search techniques can result in mis identification with low quality matches and limited confidence in the result

TargetView software

The way forward….

- Development of data mining software which looks more intensively at the GCMS data
- Implementation of spectral deconvolution to clean merged analyte/matrix spectra
- The application of multivariate data analysis algorithms provides an orthoganol dimension of analysis

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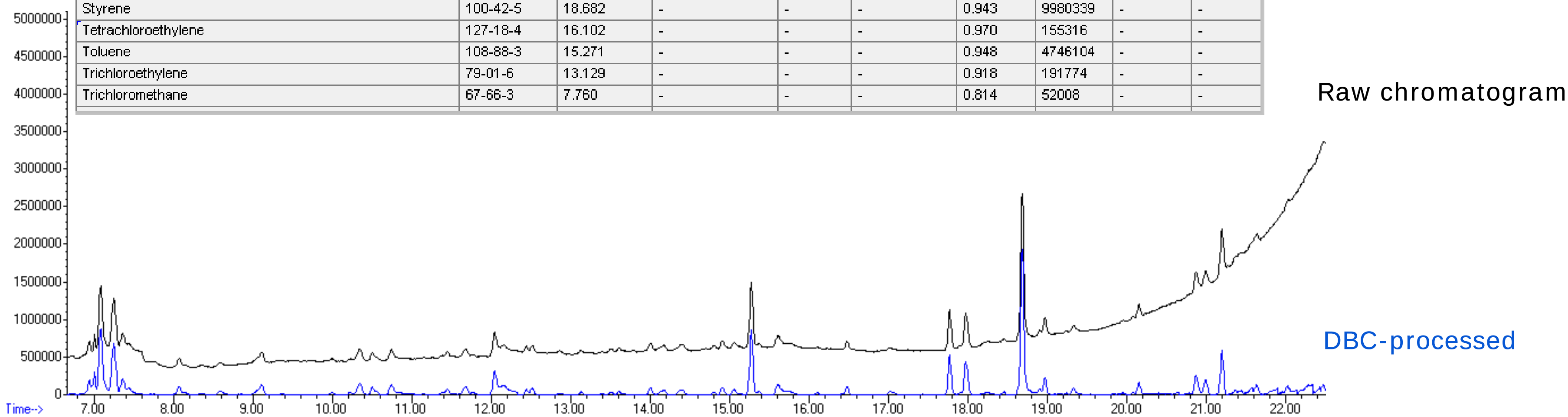
Data Analysis using TargetView software

Target compound	CAS no.	Retention time (mins)	Expected retention time (mins)	delta RT (seconds)	Retention index library	Matching coefficient	Peak sum (TIC)	Peak sum (extr. ion)	Extracted ion
2-Butanone	78-93-3	10.504	-	-	-	0.824	737923	-	-
Acetone	67-64-1	7.084	-	-	-	0.916	5385525	-	-
Benzene	71-43-2	12.044	-	-	-	0.949	2806190	-	-
Benzene, 1,3-dichloro-	541-73-1	21.635	-	-	-	0.919	650369	-	-
Benzene, 1,3-dimethyl-	108-38-3	17.972	-	-	-	0.947	2839083	-	-
Benzene, 1-ethyl-4-methyl-	622-96-8	20.073	-	-	-	0.817	120012	-	-
Dichlorodifluoromethane	75-71-8	3.493	-	-	-	0.933	2271907	-	-
Ethane, 1,1,2-trichloro-1,2,2-trifluoro-	76-13-1	6.972	-	-	-	0.913	810621	-	-
Ethanol	64-17-5	6.164	-	-	-	0.892	1065482	-	-
Ethylbenzene	100-41-4	17.767	-	-	-	0.951	2826414	-	-
Heptane	142-82-5	12.442	-	-	-	0.940	281461	-	-
Hexane	110-54-3	9.114	-	-	-	0.949	808826	-	-
Isopropyl Alcohol	67-63-0	7.364	-	-	-	0.864	1471031	-	-
Methylene Chloride	75-09-2	8.082	-	-	-	0.865	378759	-	-
Styrene	100-42-5	18.682	-	-	-	0.943	9980339	-	-
Tetrachloroethylene	127-18-4	16.102	-	-	-	0.970	155316	-	-
Toluene	108-88-3	15.271	-	-	-	0.948	4746104	-	-
Trichloroethylene	79-01-6	13.129	-	-	-	0.918	191774	-	-
Trichloromethane	67-66-3	7.760	-	-	-	0.814	52008	-	-



Chromatogram of semi-rural air sample, before and after DBC processing. The inset shows TargetView report of those TO-15 / 17 compounds positively identified in the sample

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Dynamic Background Compensation (DBC)

- **Dynamic Background Compensation (DBC) is a sophisticated software algorithm designed to distinguish between chromatographic peaks and slower GC-background / baseline anomalies.**

The main advantages of DBC include:

- **Improved spectral purity**

  - Enhanced identification of trace target analytes and unknowns.

- **Selective elimination of interfering ions resulting in**

  - Flat chromatographic baseline

  - Enhanced integration

- **Increased sensitivity**

  - Reduced noise enhances S/N

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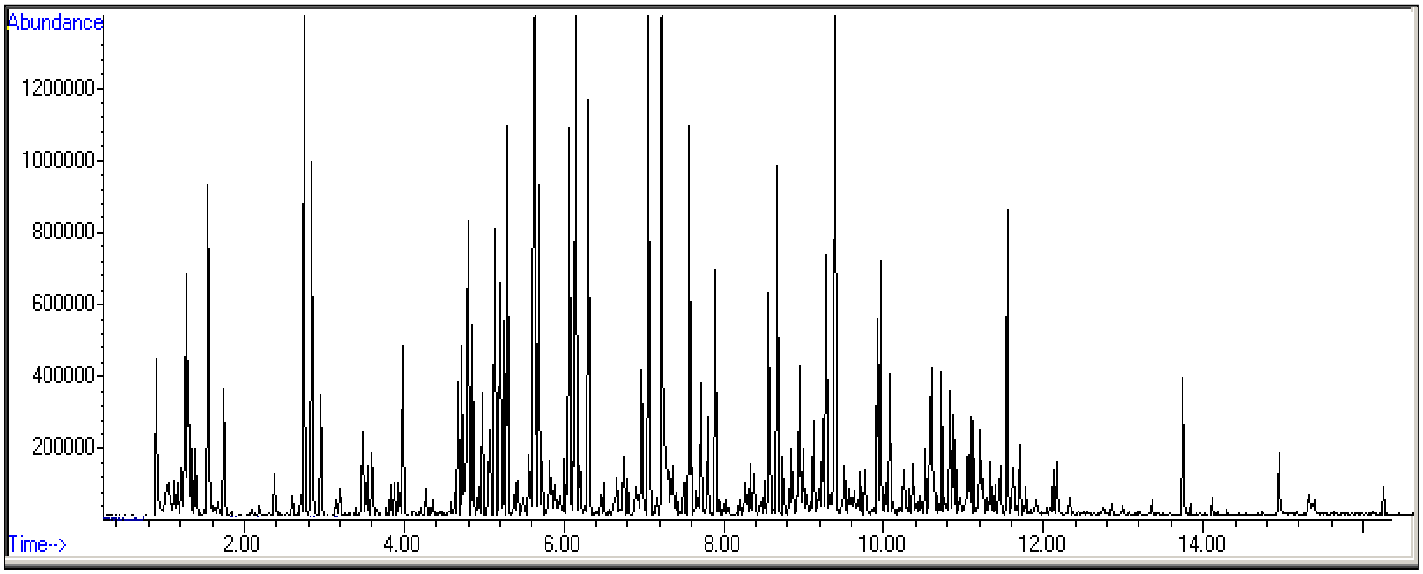
DBC in action –

Baseline noise suppression



Post DBC – baseline optimised, minimal background noise

Original – non background compensated GCMS (TIC) data

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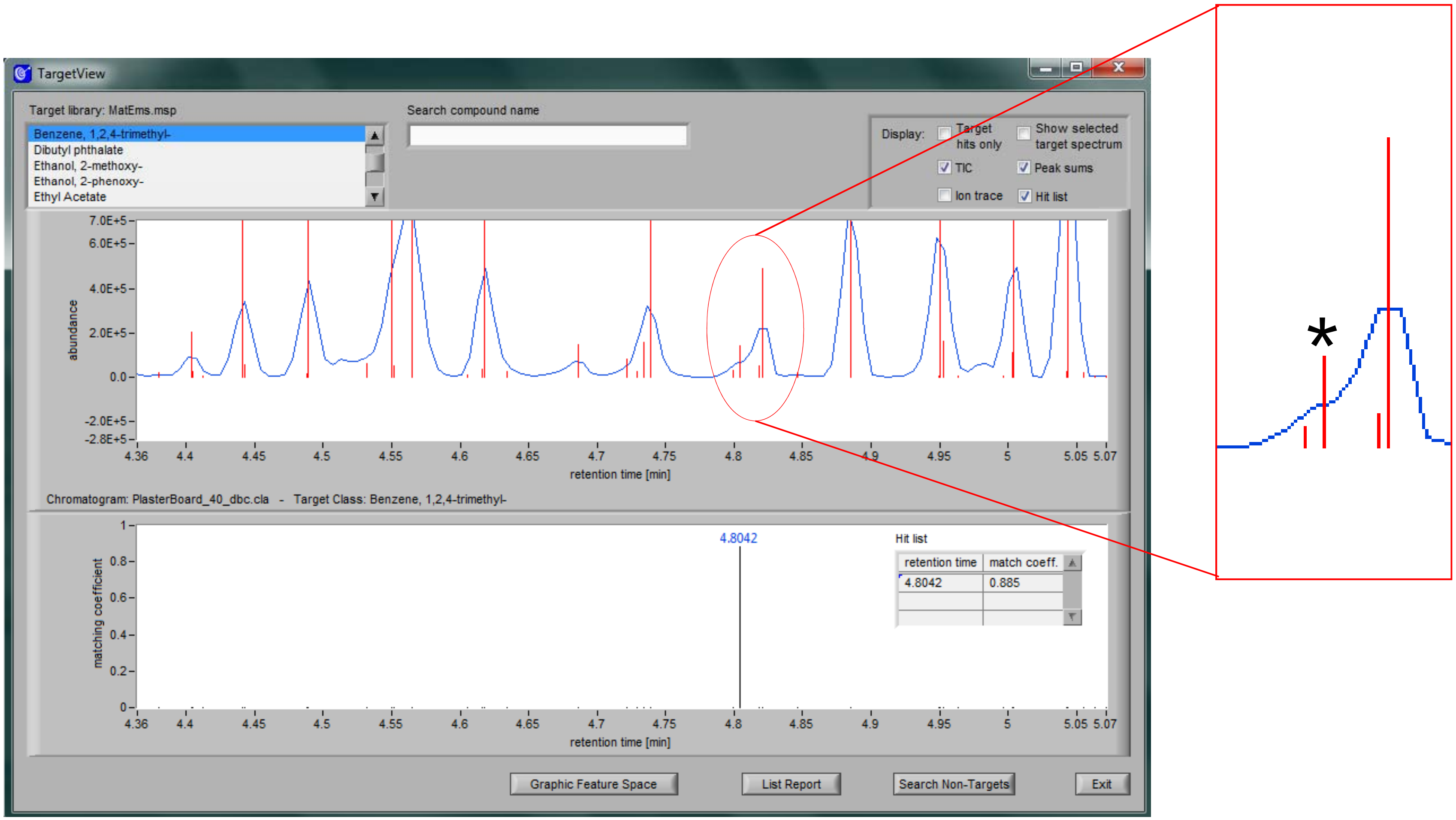
Deconvolution of peaks



Deconvolved spectra for both known and unknown compounds can be cross searched against NIST databases

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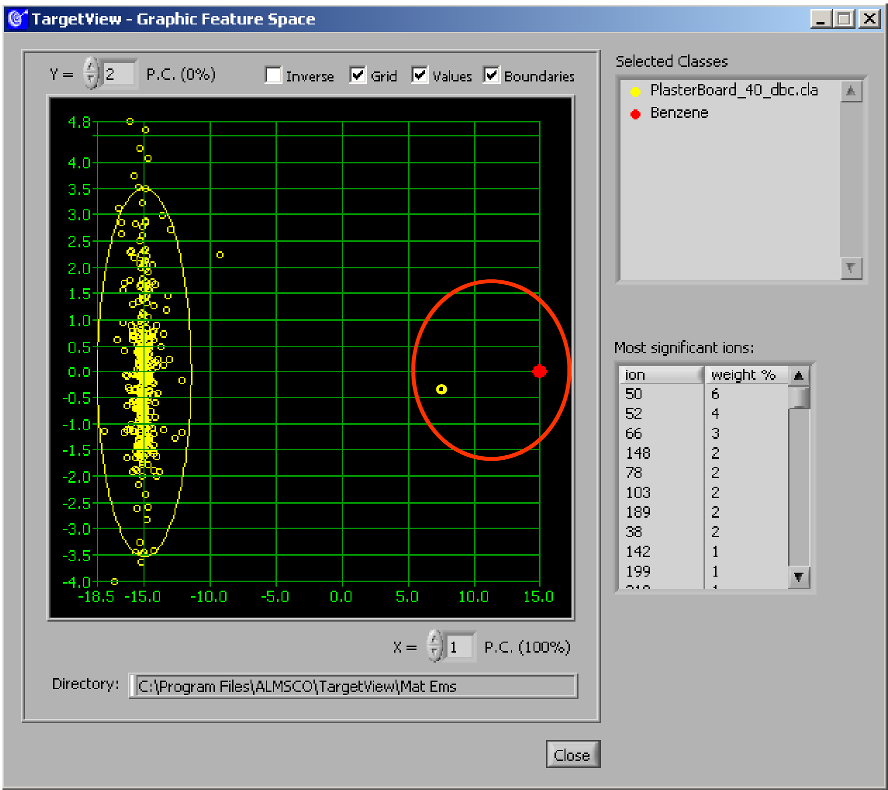
The chemometric visualisation of data (PCA)



PCA identification of benzene

- **Deconvolution identifies a number of target and unknown compounds in the sample**
- **The deconvolved spectrum for all compounds (yellow circles) is projected onto a 2 dimensional plane.**
- **The red dot equates to the target compound spectrum**
- **Proximity of a yellow circle to the target indicates a positive hit**

The close proximity of 1 spectrum indicates a single positive match

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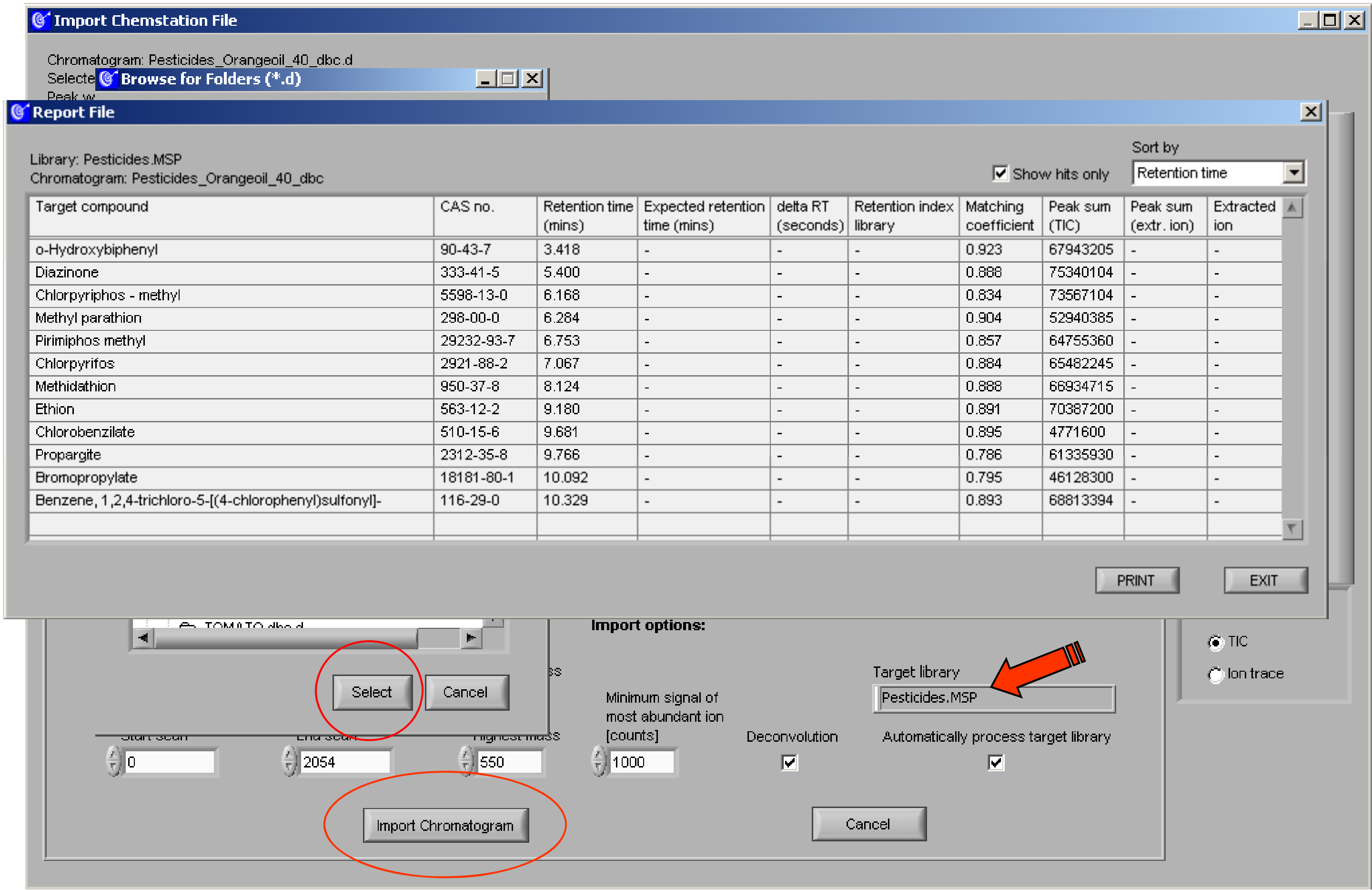
Simplicity of use -

Generating a TargetView report is just a 2 step process

1) Select a data file 2) Import the data and print a report



Target compound	CAS no.	Retention time (mins)	Expected retention time (mins)	delta RT (seconds)	Retention index library	Matching coefficient	Peak sum (TIC)	Peak sum (extr. ion)	Extracted ion
o-Hydroxybiphenyl	90-43-7	3.418	-	-	-	0.923	67943205	-	-
Diazinone	333-41-5	5.400	-	-	-	0.888	75340104	-	-
Chlorpyriphos - methyl	5598-13-0	6.168	-	-	-	0.834	73567104	-	-
Methyl parathion	298-00-0	6.284	-	-	-	0.904	52940385	-	-
Pirimiphos methyl	29232-93-7	6.753	-	-	-	0.857	64755360	-	-
Chlorpyrifos	2921-88-2	7.067	-	-	-	0.884	65482245	-	-
Methidathion	950-37-8	8.124	-	-	-	0.888	66934715	-	-
Ethion	563-12-2	9.180	-	-	-	0.891	70387200	-	-
Chlorobenzilate	510-15-6	9.681	-	-	-	0.895	4771600	-	-
Propargite	2312-35-8	9.766	-	-	-	0.786	61335930	-	-
Bromopropylate	18181-80-1	10.092	-	-	-	0.795	46128300	-	-
Benzene, 1,2,4-trichloro-5-[(4-chlorophenyl)sulfonyl]-	116-29-0	10.329	-	-	-	0.893	68813394	-	-

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Summary

- A combination of canisters and sorbent tubes provides a comprehensive evaluation of an application, e.g. ambient air monitoring
- BenchTOF-dx provides a sensitivity and productivity boost that can be utilised several ways while providing method tunes and NIST-compliant spectra
- Challenges associated with identifying target compounds in complex GCMS profiles can now be overcome by employing simple data analysis packages such as TargetView.

Any Questions?

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