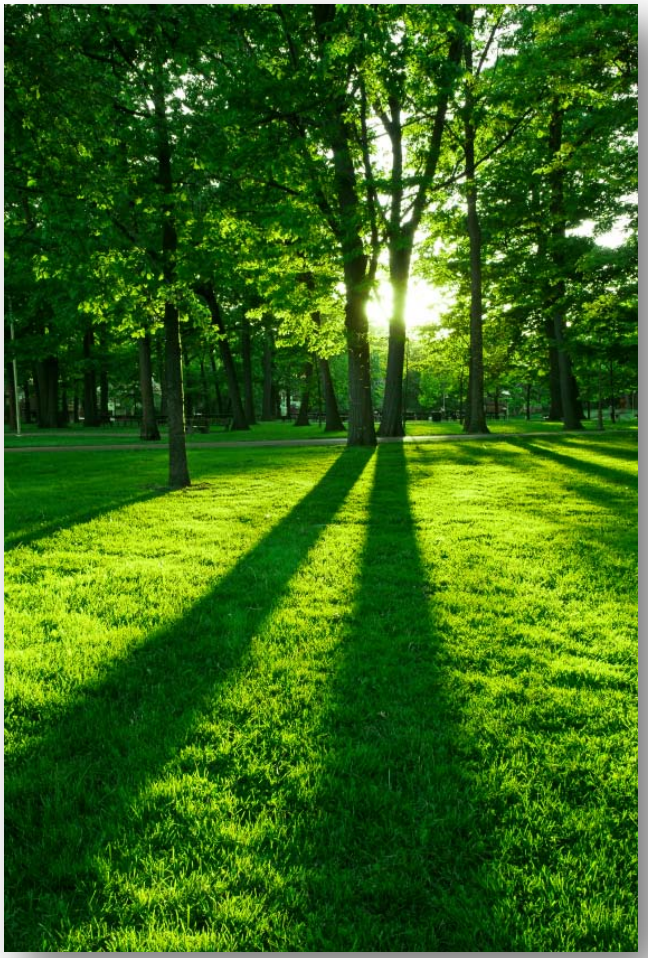
Making Tube Sampling Easy: the Development of a New Type of "Grab Sampler "

Nicola Watson
nwatson@markes.com



MARKES international

National Environmental Monitoring Conference,
Bellevue, WA, August 2011

Agenda

- Overview of sample collection and analysis
  - Focus canister sampling
  - Focus Sorbent tubes
- Objections against sorbent tubes
- Development of an easy sampling device
  - Synergy with Time-of-Flight detectors

The Thermal Desorption Process

On-line

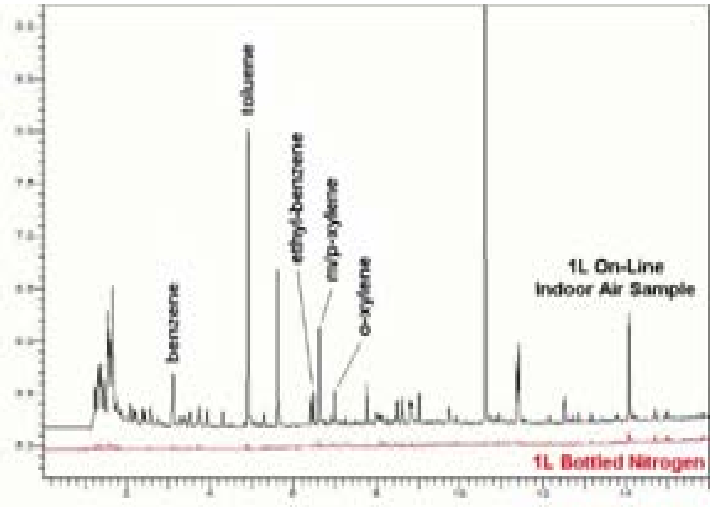
Direct desorption of materials

Canisters/Bags

Sorbent Tubes

Headspace …

Electrically-cooled focusing trap



100-200 µL injection of vapour into GC(MS)

Water and volatile interferences may be purged to vent

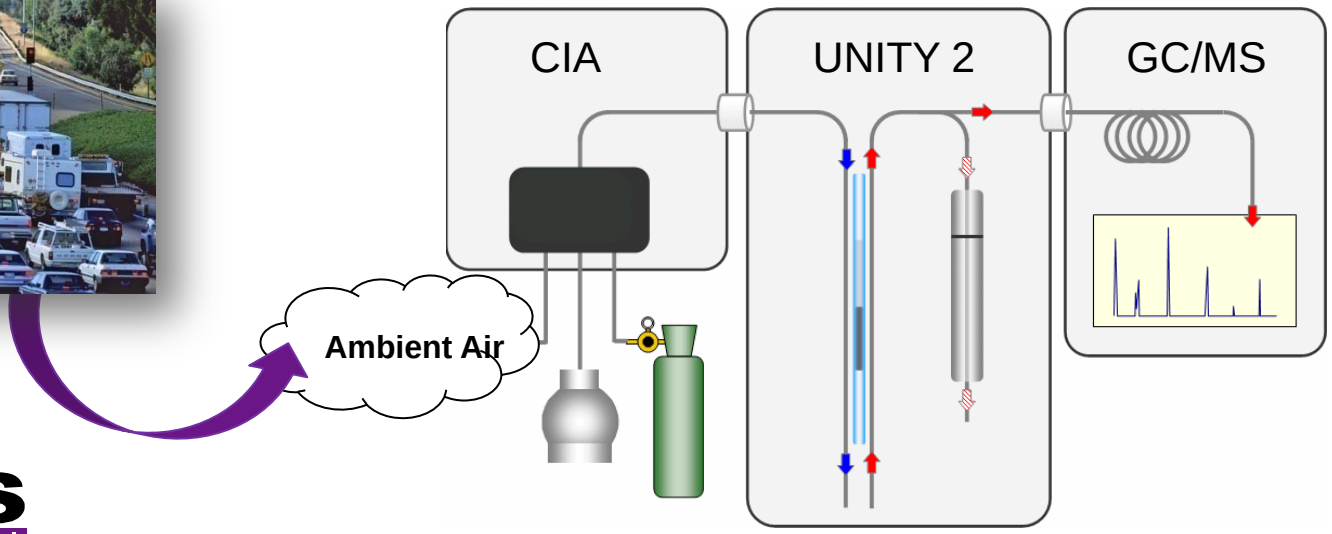
MARKES international

www.markes.com

Canister analysis methods (*e.g.* US EPA TO-15)

Method summary

- Grab sampling using canisters is easy, TWA monitoring is not
- Samples may be stored for up to 30 days
- A small volume of air from the canister (typically ~500 mL) can be introduced straight to the focusing trap of the desorber
- Trapping conditions are set such that water is selectively eliminated during the trapping process.
- Analysis by GC/MS in scan or SIM mode

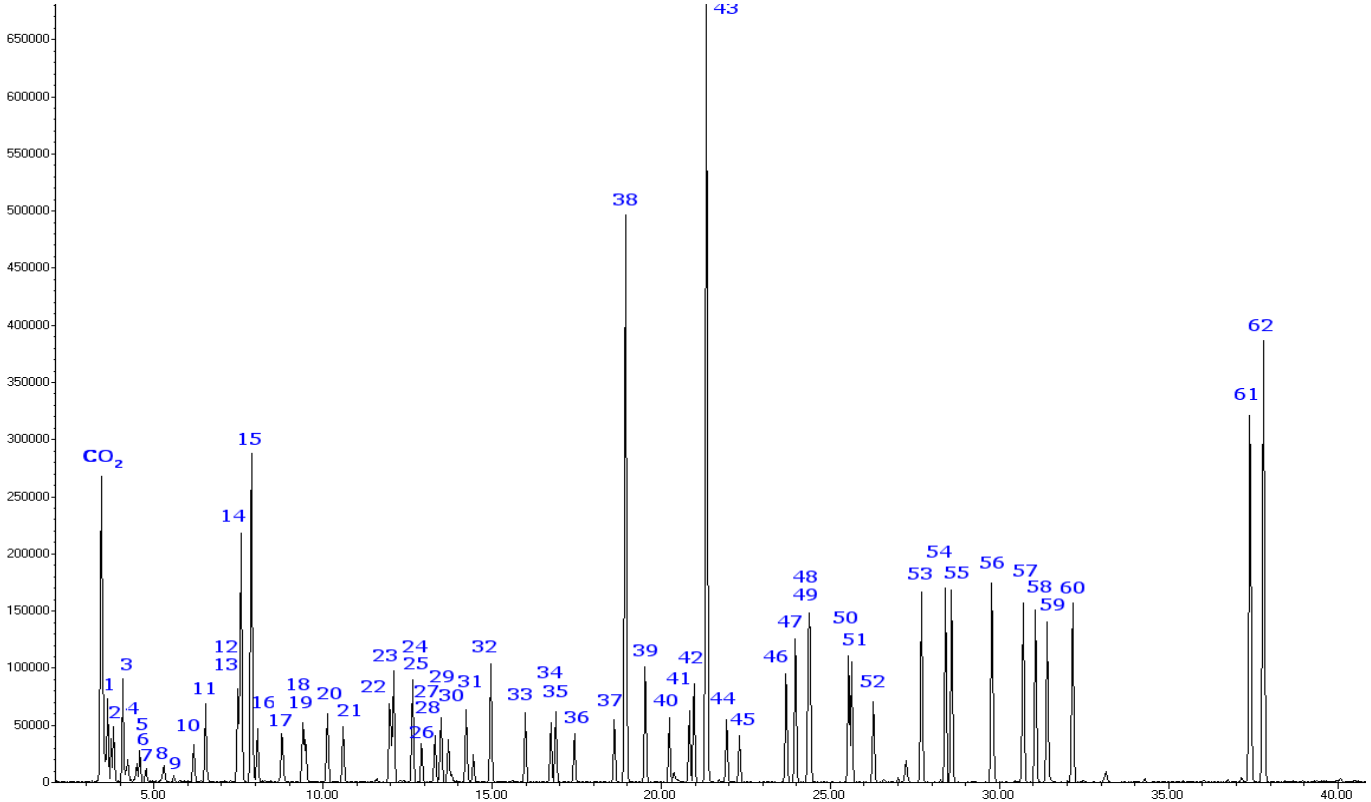


MARKES international

‘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 UNITY-CIA 8



Source: TDTS 81

MARKES international

Air monitoring: Canisters or tubes?

Use canisters:

1. For ultra-volatiles
2. For non-polar compounds
3. Preferably at trace levels
4. *When you have to*

Canister limitations

1. Expense (€500 -1000 each)
2. Poor recovery of anything higher boiling than Xylene
3. Cleaning needs expensive vacuum equipment, at least 3 cleaning cycles and verification with GC/MS

MARKES international

www.markes.com

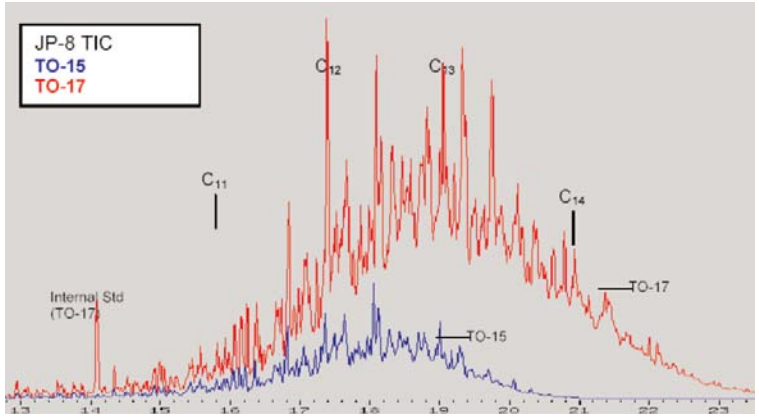
Canisters or tubes?

	Tubes	Canisters
Perception	World-wide acceptance	Gold standard for US ambient air market
Applications	Ambient air, indoor air, vapor intrusion, industrial hygiene Material emissions Food & flavor Chemical weapons	Ambient air, indoor air, vapor intrusion, emergency response
Handling	Light weight for personal monitoring and general ease of use	Larger and heavier; more costly to ship
Sampling	C_3- C_{40} Concentration range ppt to %	C_2-C_{10} Concentration range ppt to low ppm
Cleaning	Analytical process automatically cleans tube for re-use	Canister cleaning requires separate equipment as additional step prior to background certification and sampling.
Cost	$50 – $130 each	$200 - $700 each

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)



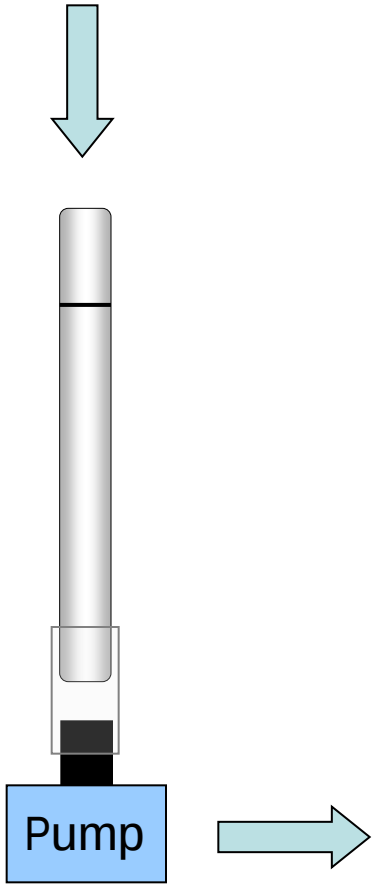
Data courtesy of H. Hayes, Air Toxics

MARKES international

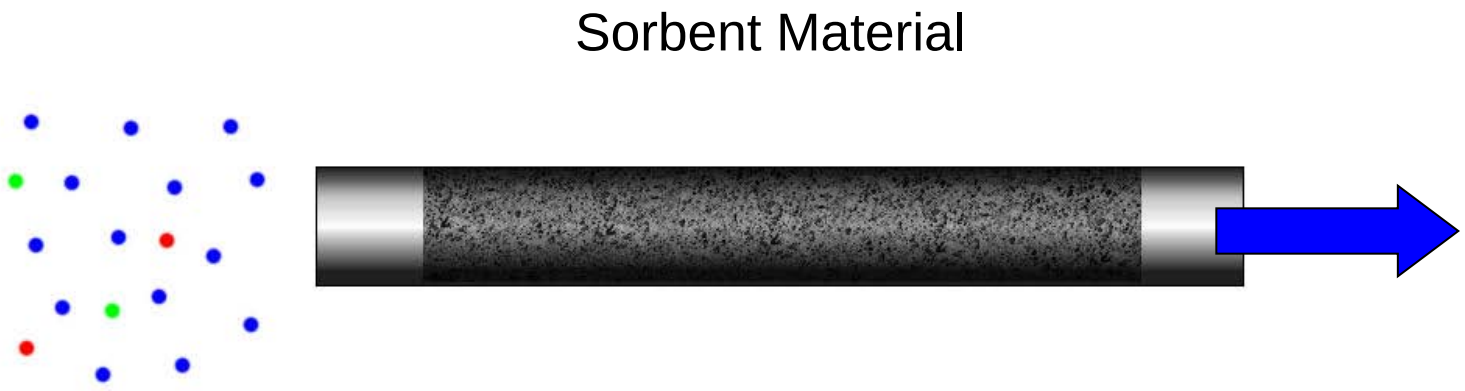
www.markes.com

Active (Pumped) Sampling

- Pump air through sorbent tube
- Flow Rate = 20 – 100 ml/min
- Volume = 500 ml – 100 L
- Much faster technique compared to diffusive sampling
- Important do not exceed breakthrough volume for a compound on a given sorbent



Tube Based Thermal Desorption – An Overview of the process



Sample Matrix

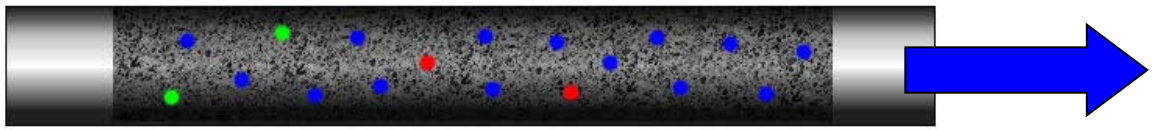
e.g. Air

MARKES international

www.markes.com

Tube Based Thermal Desorption

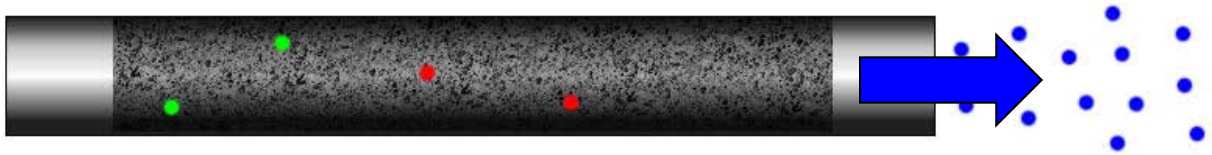
Sample passes onto the sorbent



Compounds of interest are adsorbed on the sorbent surface

MARKES international

Tube Based Thermal Desorption



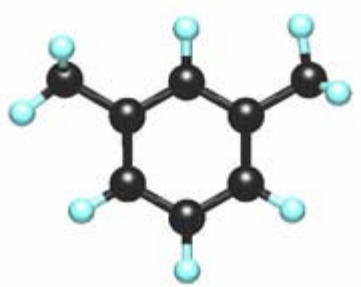
Lighter gases such as nitrogen pass through the sorbent

MARKES international

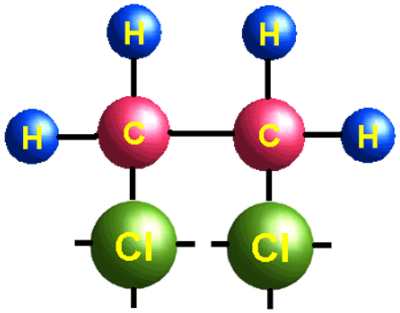
Air Monitoring - Pumped

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



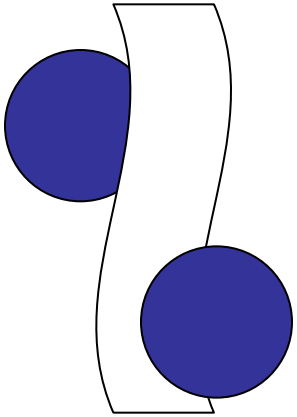
MARKES international

Sorbent selection

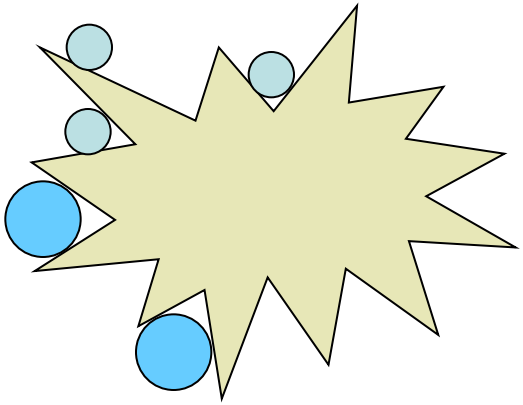
The sorbent(s) selected must quantitatively retain the compounds of interest from the volume of air / gas sampled ***and*** must then release those compounds as efficiently as possible during the desorption process.

Sorbent selection principally depends upon the volatility of the analyte(s) concerned –***the more volatile the analyte to be trapped, the stronger the sorbent must be.***

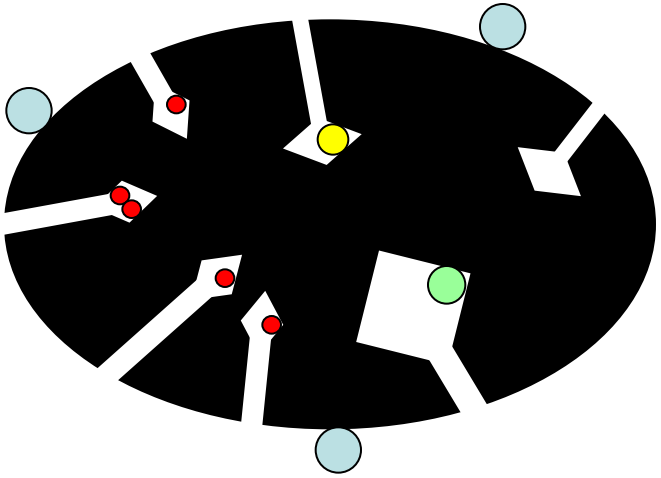
Quartz Wool



Porous Polymer



Carbon Molecular Sieve

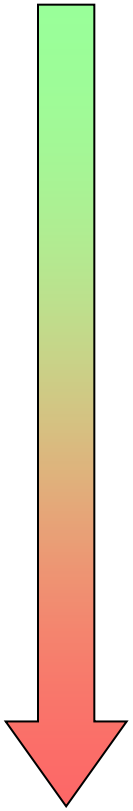


MARKES international

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}
Carbopack X	$C_{3/4}$ - $C_{6/7}$
UniCarb	C_3 - C_8
Carboxen 1000	C_2-C_5
Carbosieve SIII	C_2-C_5

Water retention

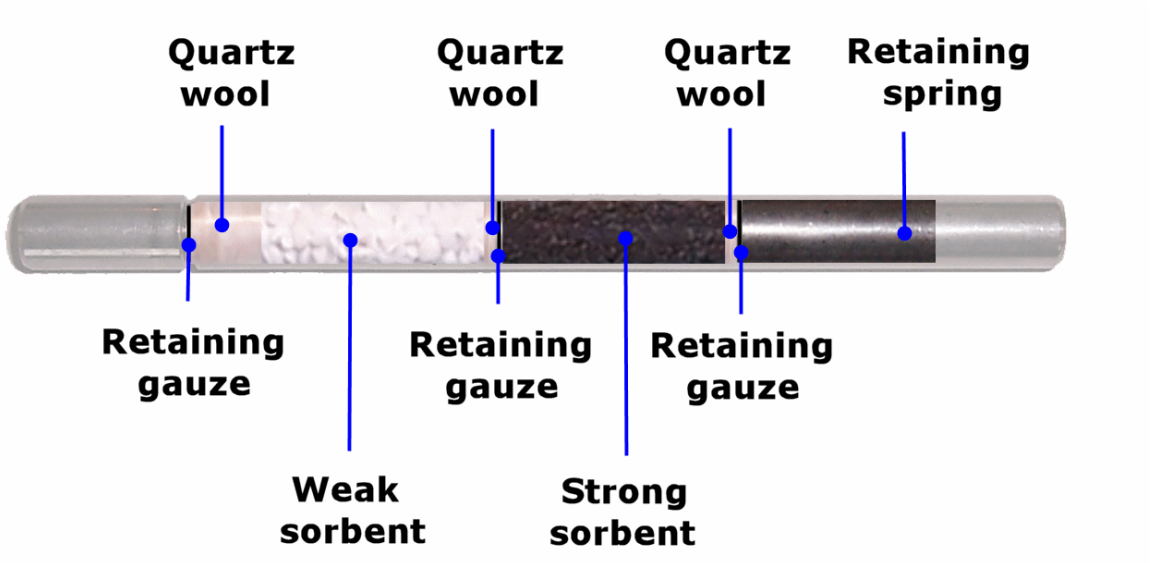


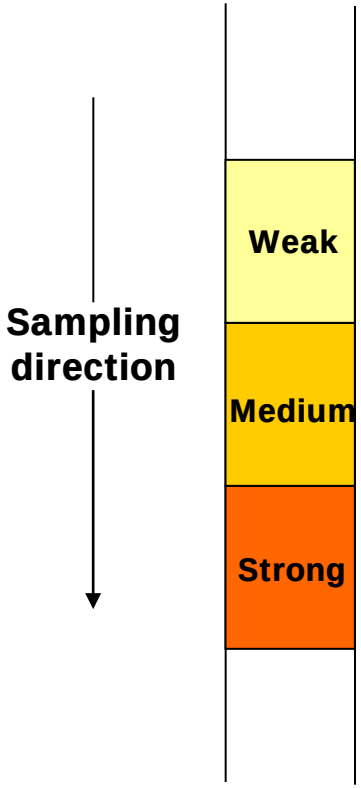
MARKES international

Air Monitoring - Pumped

What if you have a wide range of compounds you wish to trap?

Answer: Use multiple sorbent beds



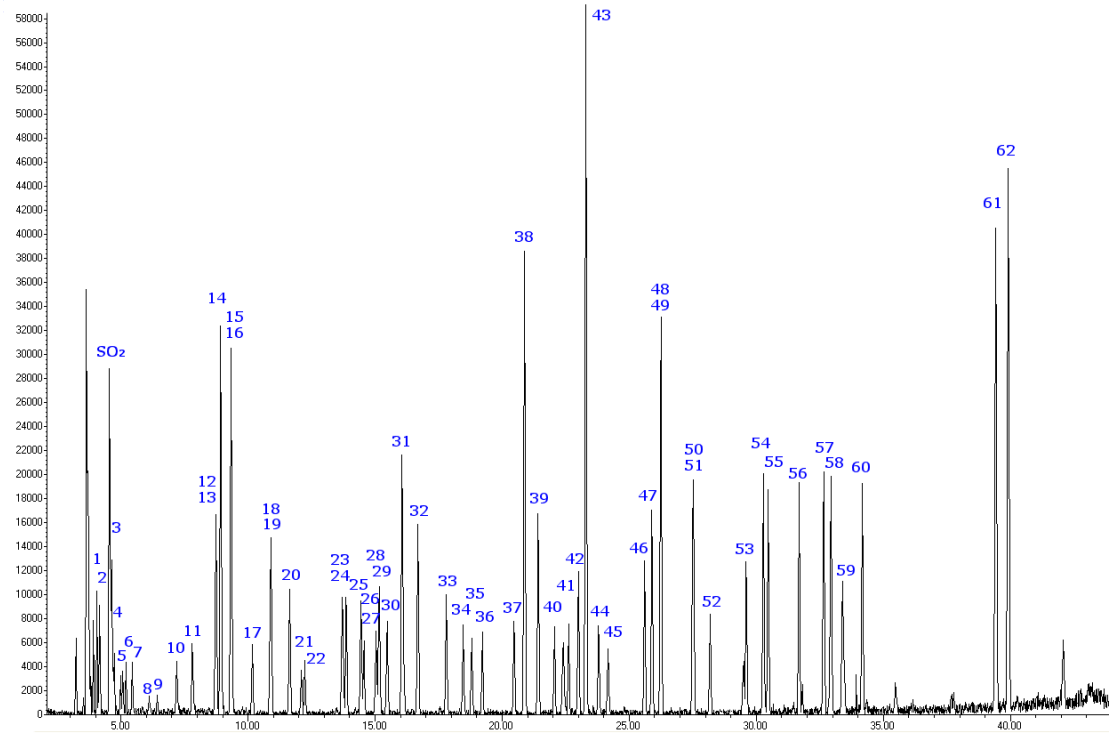


MARKES international

‘Air toxics’ on sorbent tubes: US EPA Method TO-17

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

Splitless desorption of ‘Air Toxics’ tube loaded with 1 L of 1 ppb std



Source: TDTS 86

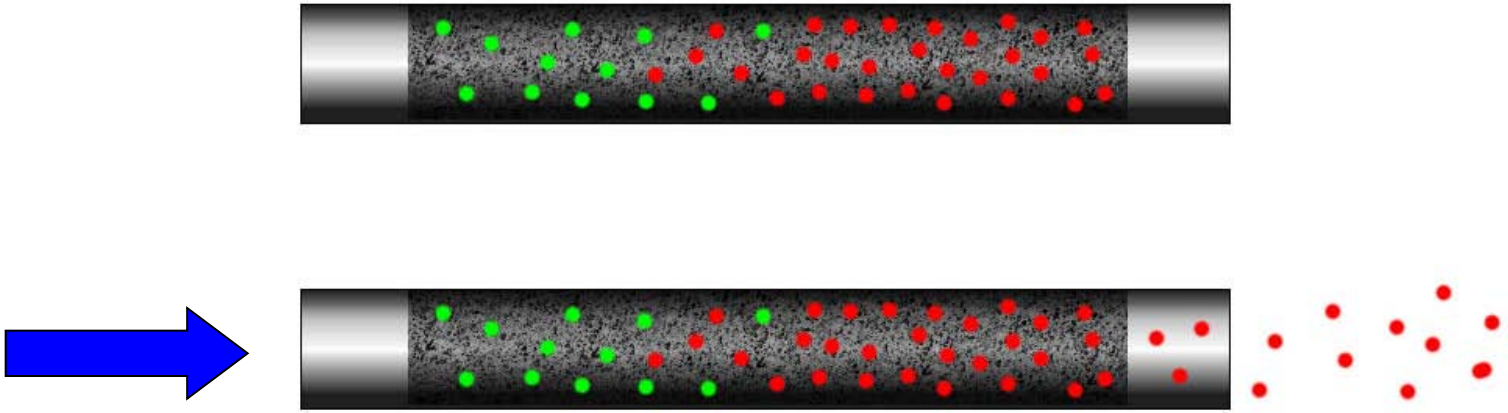
MARKES international

www.markes.com

Objections

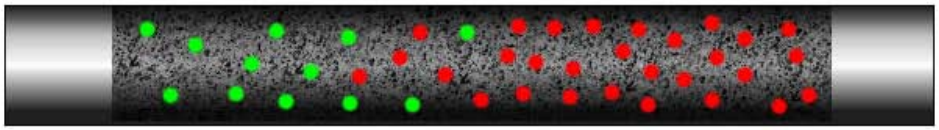
- What about breakthrough?

Breakthrough



Sample volume;

lower volume = less risk of breakthrough



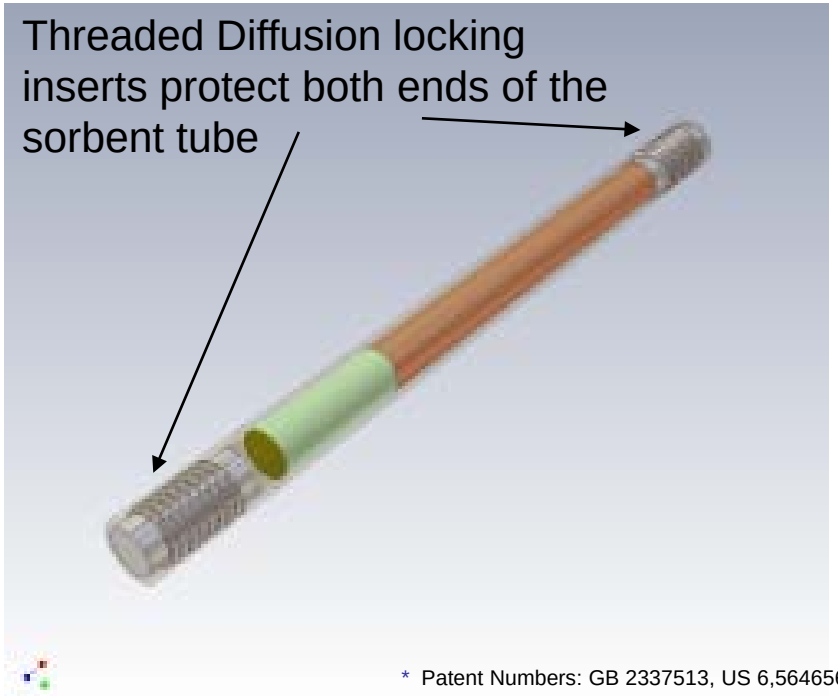
Objections

- What about breakthrough?
- Capping and secure shipment of the tubes.

Tube Capping

SafeLok Tubes*

- Reduces risk of contamination
- Prevents necking caused by over tightening
- Facilitates pumped sampling at low flow rates (< 1 ml/min)
- Safer to handle tubes used to collect toxic compounds
- Same mass of sorbent and same external dimensions as standard tubes



* Patent Numbers: GB 2337513, US 6,564656 B1

MARKES international

Objections

- What about breakthrough?
- Capping and secure shipment of the tubes.
- Calibration of the pump before sampling.

Easy-VOC – Pumped tube sampling made easy

- Grab sampling for sorbent tubes: Reliable sampling of 50 or 100 ml volumes (or multiples of same)
- Kit includes: hand pump, Safelok tubes and caps.
- Main features
  - Ease of use – great for inexperienced personnel
  - Humidity effects – Negligible
  - Breakthrough? – Minimised
  - Use of SafeLok tubes and push on caps simplifies operation and prevents over tightening of storage caps

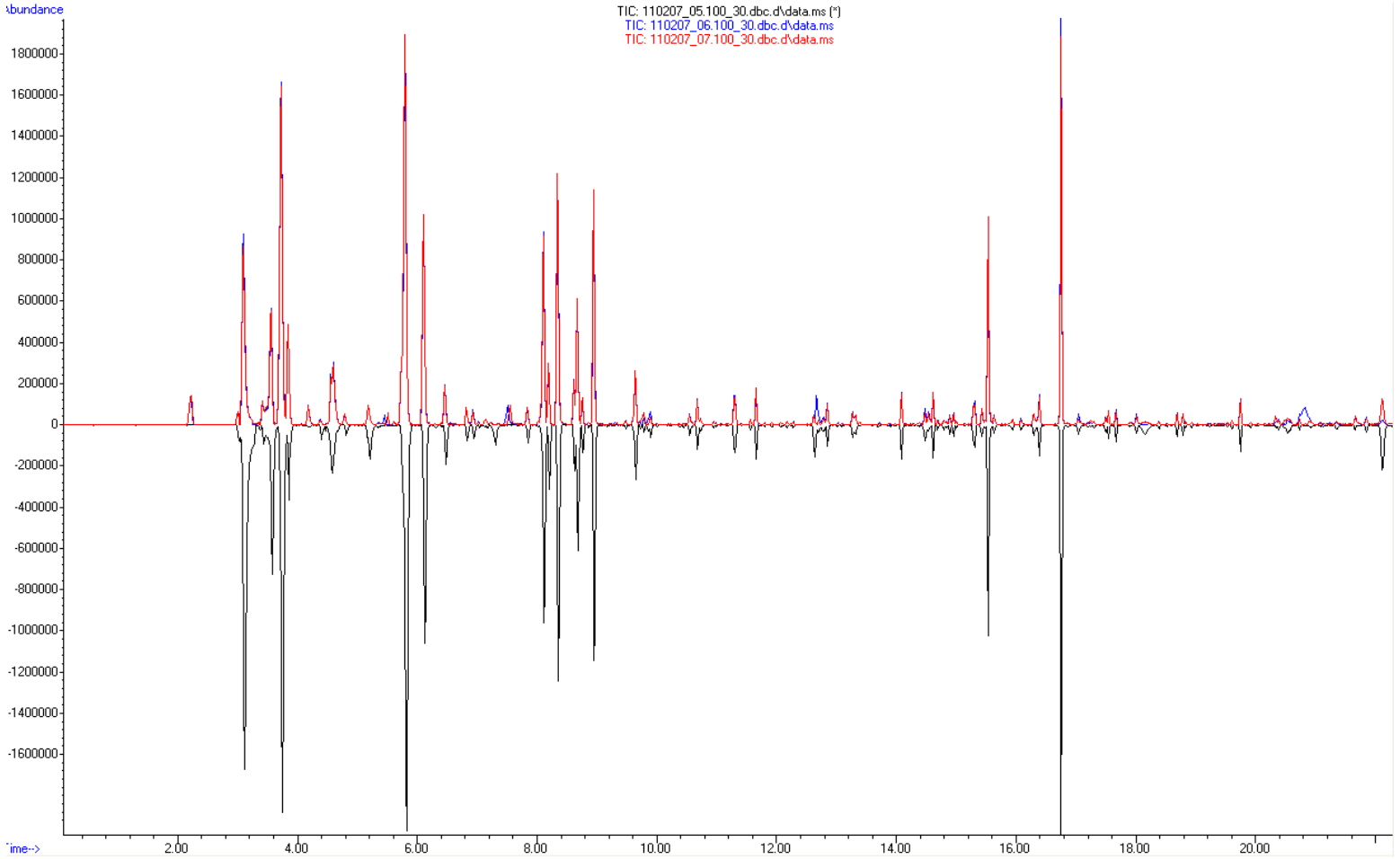
Easy-VOC *- For soil gas, workplace air & stack gas.*

Also the perfect complement to high sensitivity GC detectors

MA international

www.markes.com

Comparisons of Easy-VOC with standard pumped sampling



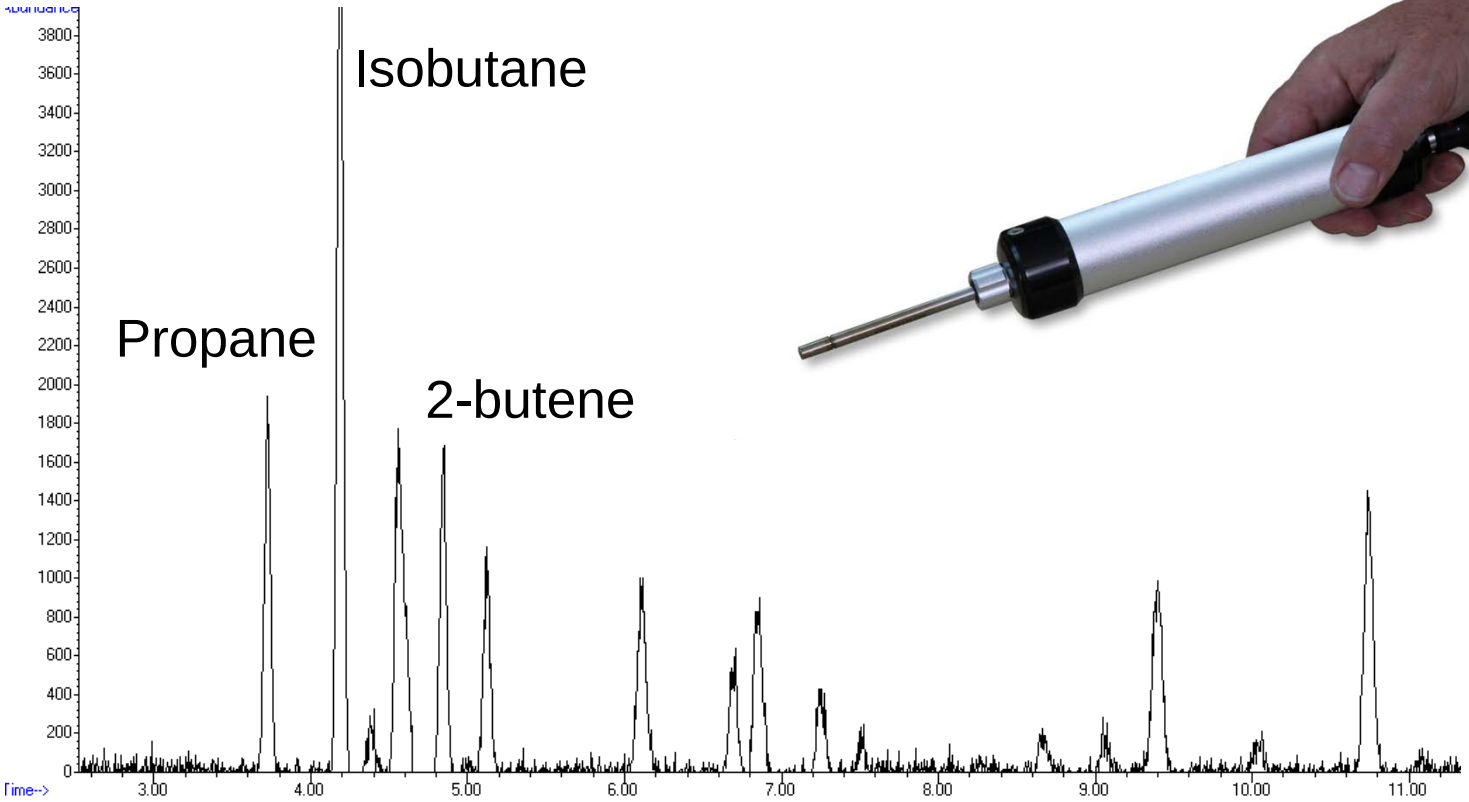
- Comparison with FLEC constant flow pump (Black) and Hand pump (Red & Blue) – equal performance

MARKES international

www.markes.com

Extending the volatility range

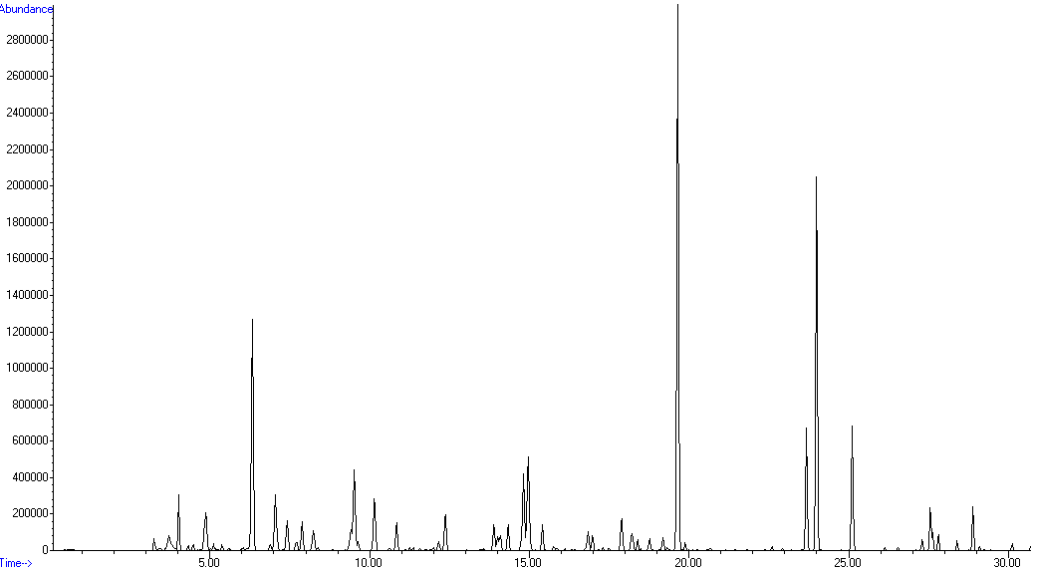
- Smaller volume less chance of breakthrough, so lighter compounds can be retained.



MARKES international

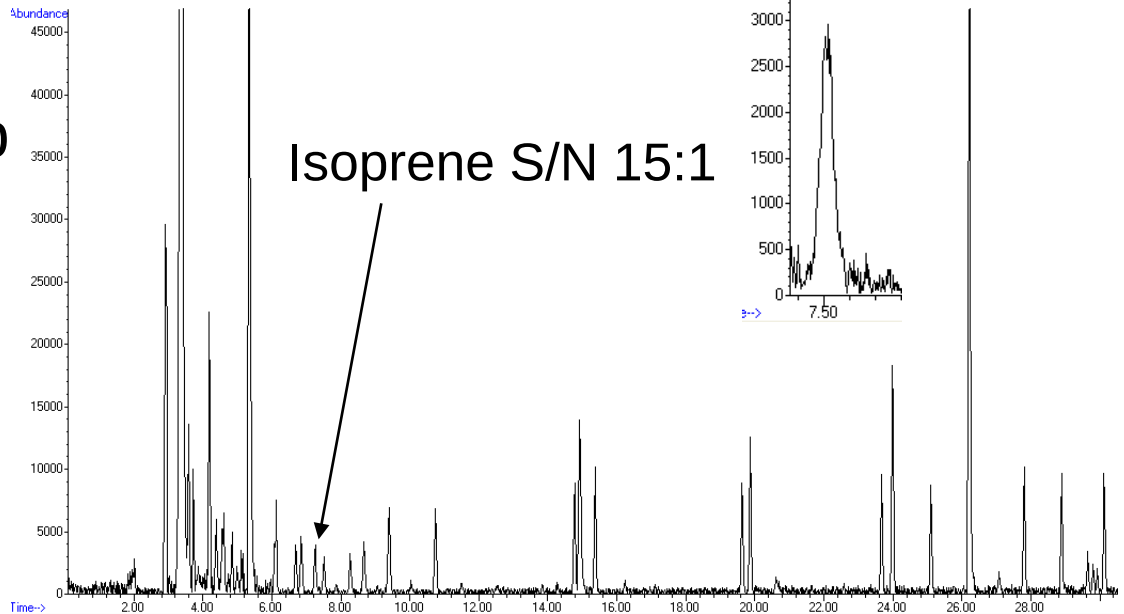
www.markes.com

Application examples; High/Low concentration



50 mL sample of diesel exhaust

500 mL sample of 4 ppb Ozone precursor standard



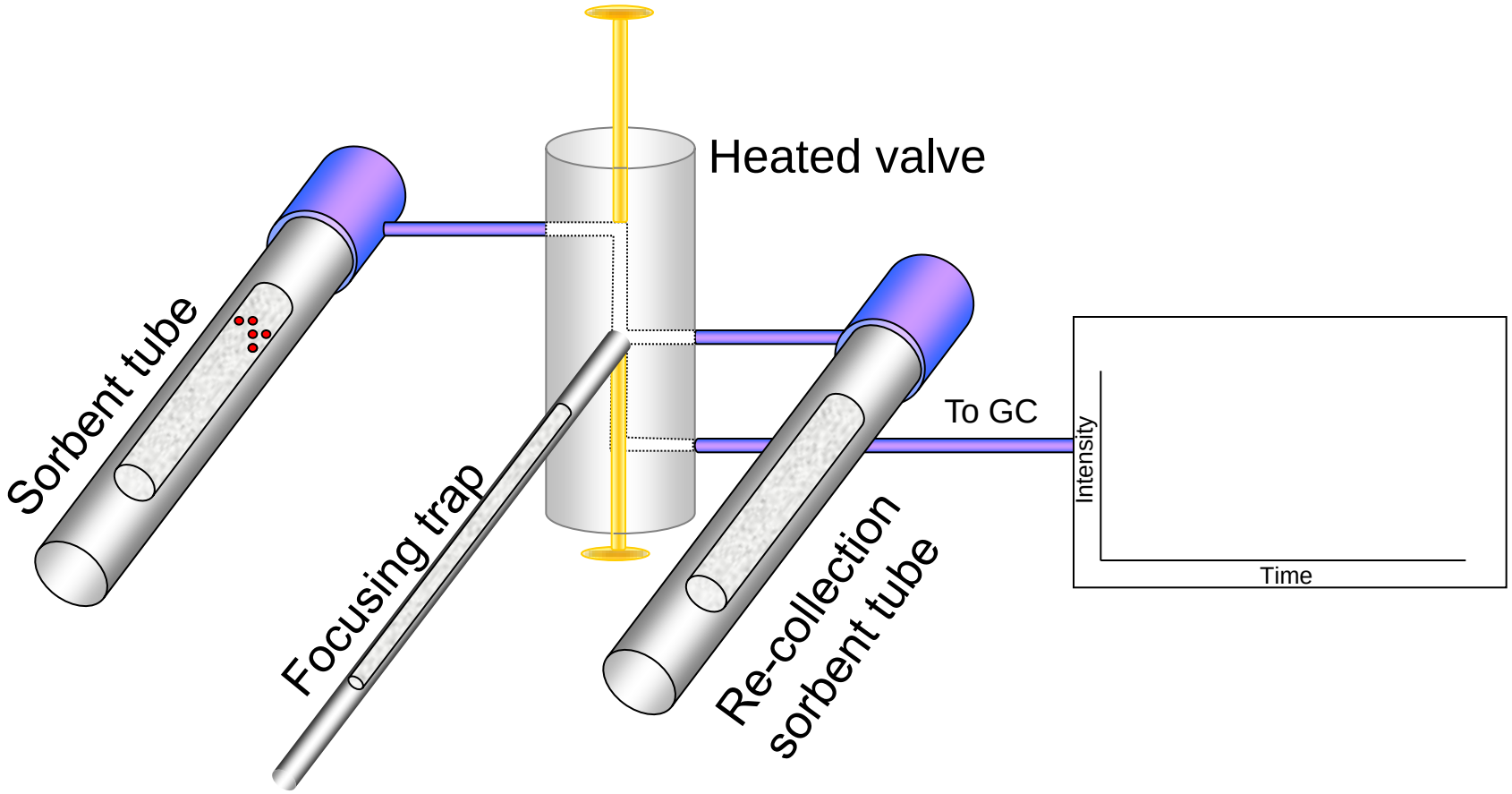
Isoprene S/N 15:1

MARKES international

www.markes.com

Sample security using sample re-collection

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

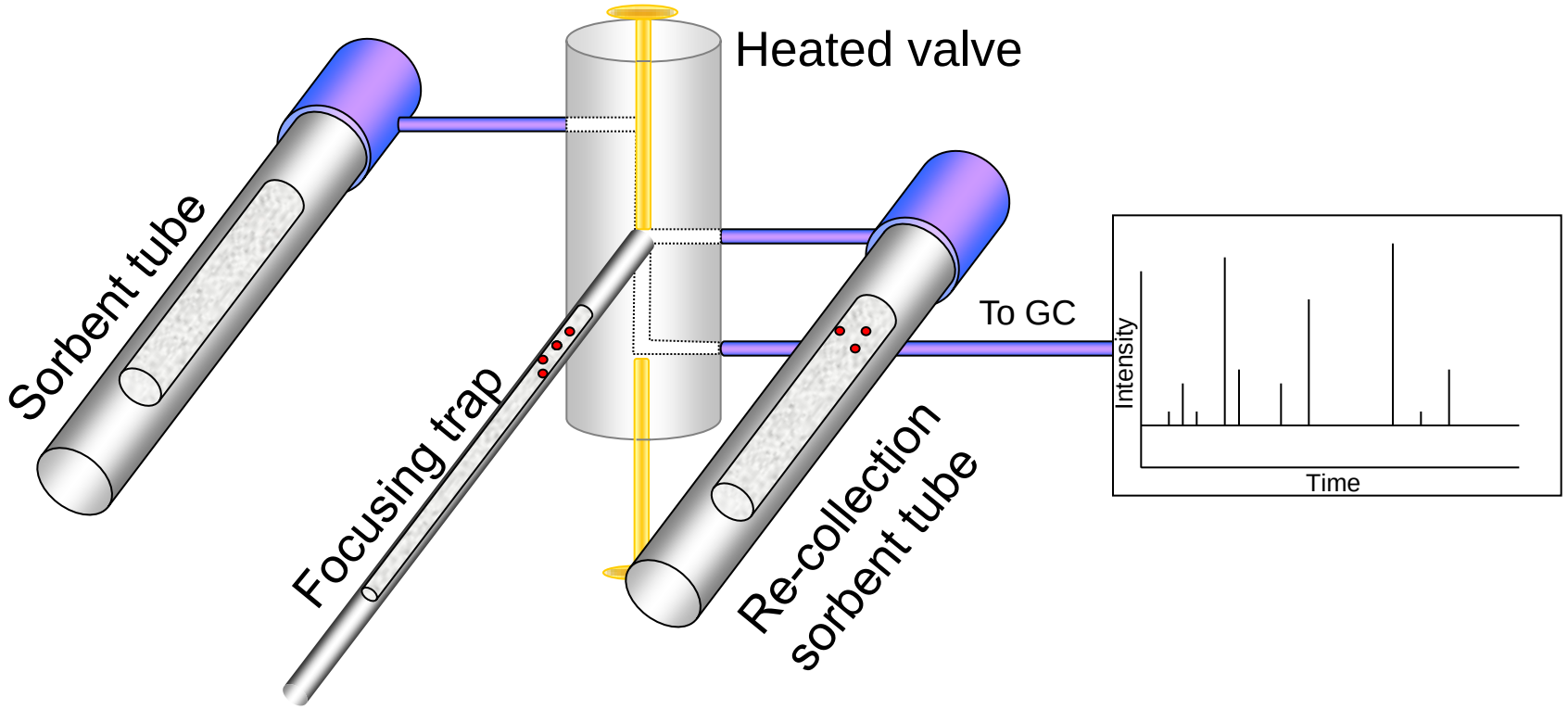


- Patented heated valve is inert and low volume: Allows quantitative recovery of high & low volatility and reactive compounds
- The heated valve isolates the TD system allowing method compliance: leak testing, backflush trap desorption, purge to vent, overlap mode, *etc.*

MARKES international

Sample security using sample re-collection

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

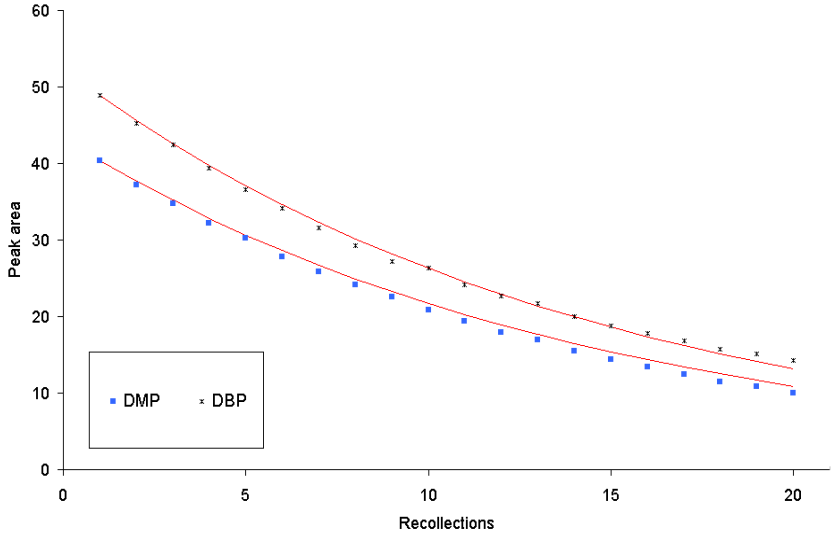


- Repeat analysis of re-collected samples makes it easy to validate analyte recovery through the TD flow path
- A change to the overall VOC profile indicates any bias

MARKES international

Using Re-collection (SecureTD-Q™)

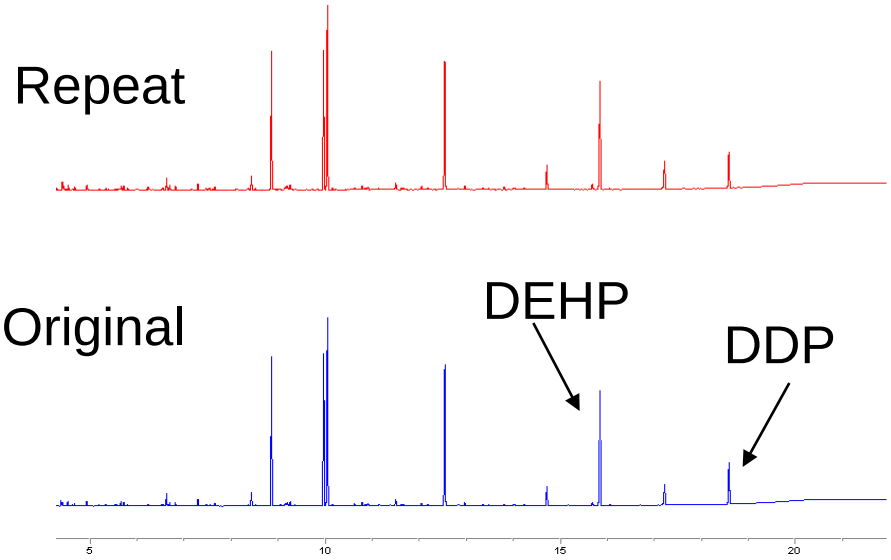
Validation of routine methods



- 2 µL phthalate solution in methanol with 21:1 single split
- 20 re-collection, repeat analyses
- **Good match between expected decay (lines) and observed decay (points)**
- **Demonstrates quantitative recovery**

Demonstrating quantitative recovery of high boilers

- Repeat desorption of a mixed phthalate std – di-ethyl- to di-n-decylphthalate
- Repeat analysis shows quantitative recovery without bias, across the analyte range



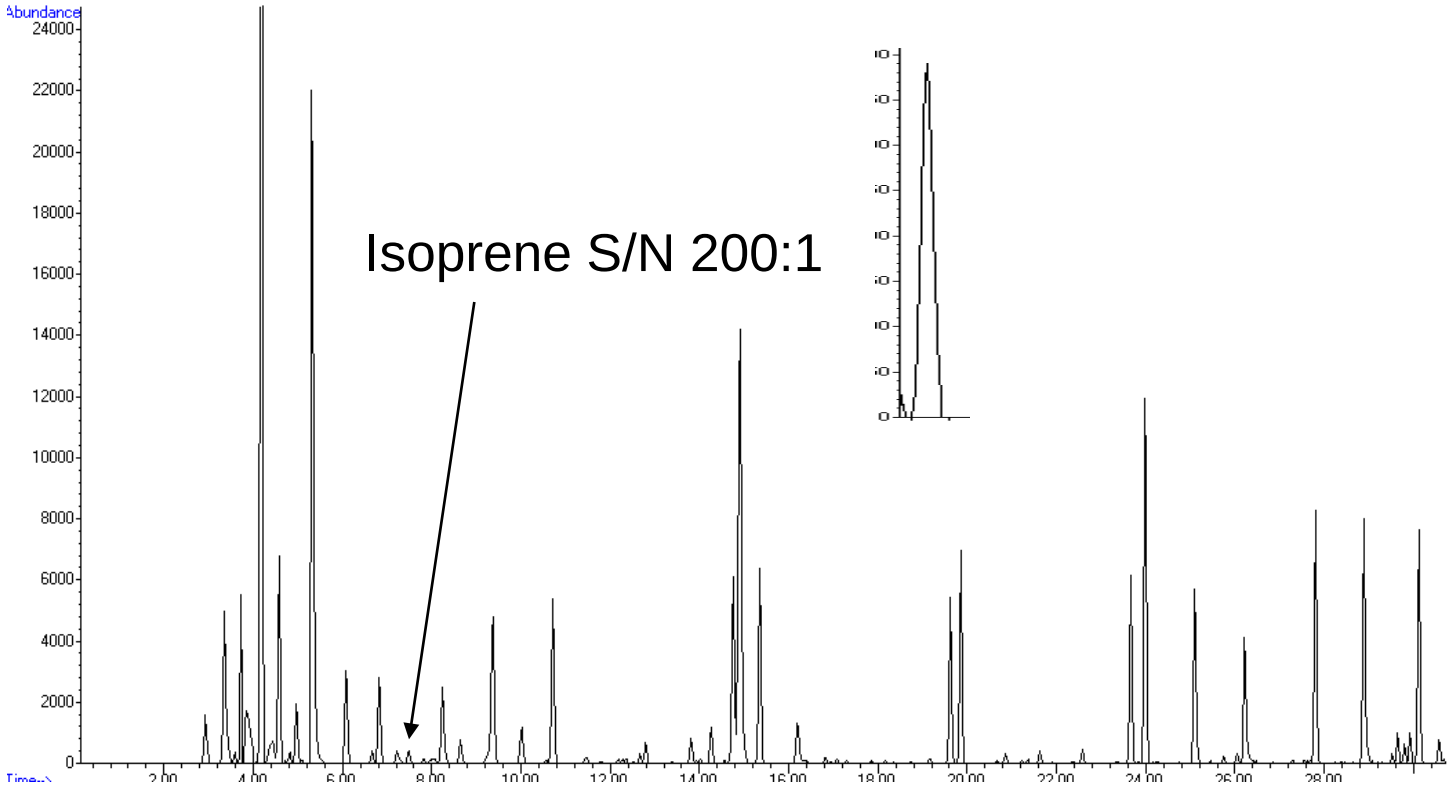
MARKES international

NB: ASTM Method D6196 references quantitative re-collection for validation

www.markes.com

Re-analysis of low concentration sample

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



MARKES international

BenchTOF-dx:
Clearer, Accurate, Selective, and Sensitive

ALMSCO international

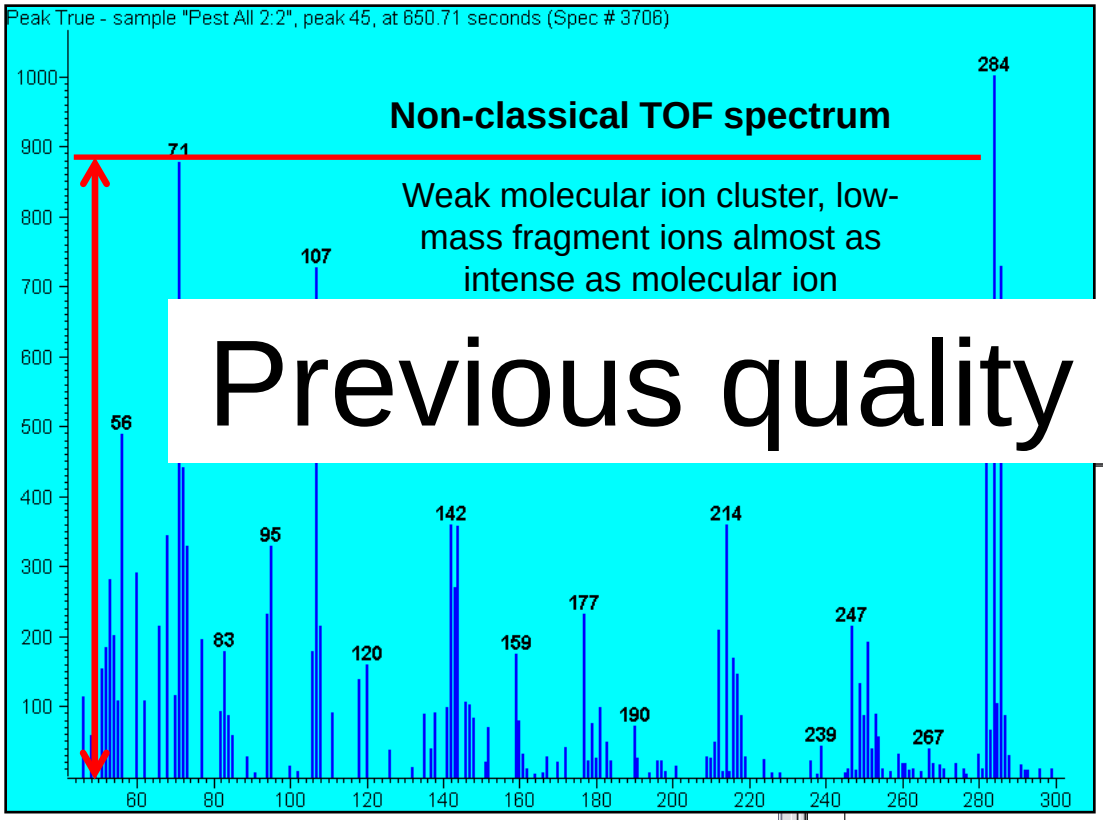
MARKES international

www.markes.com

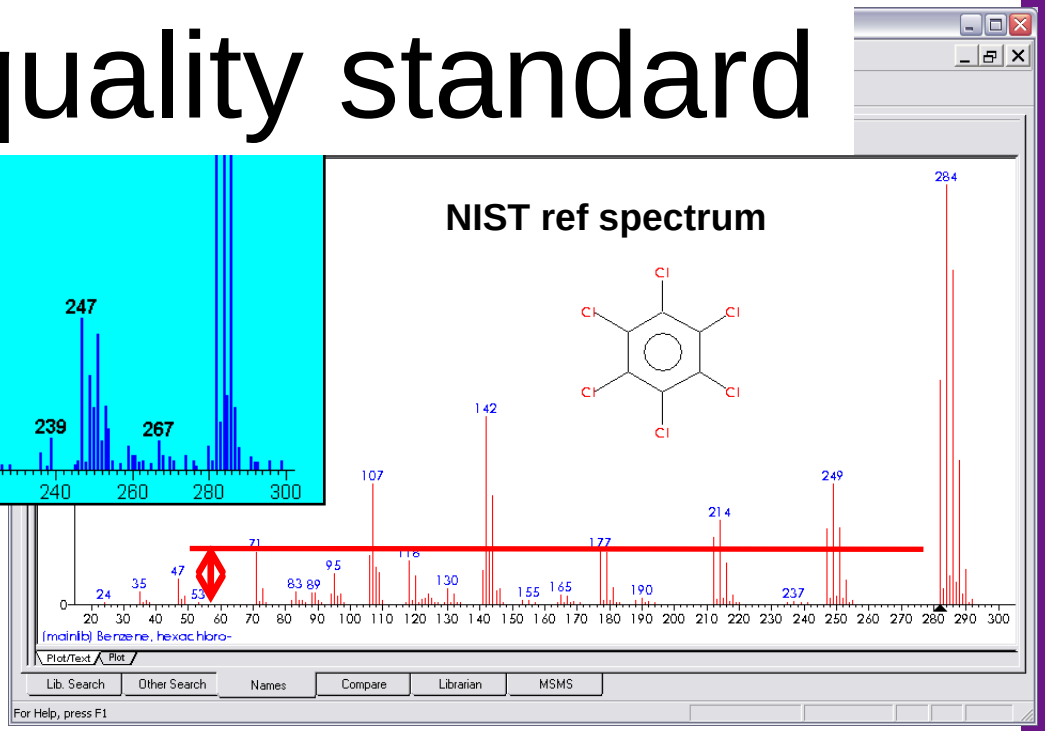
What does BenchTOF-dx offer?

- Spectral Accuracy
- Sensitivity
- Clarity
- Selectivity

Previous quality standard of HCB



Previous quality standard

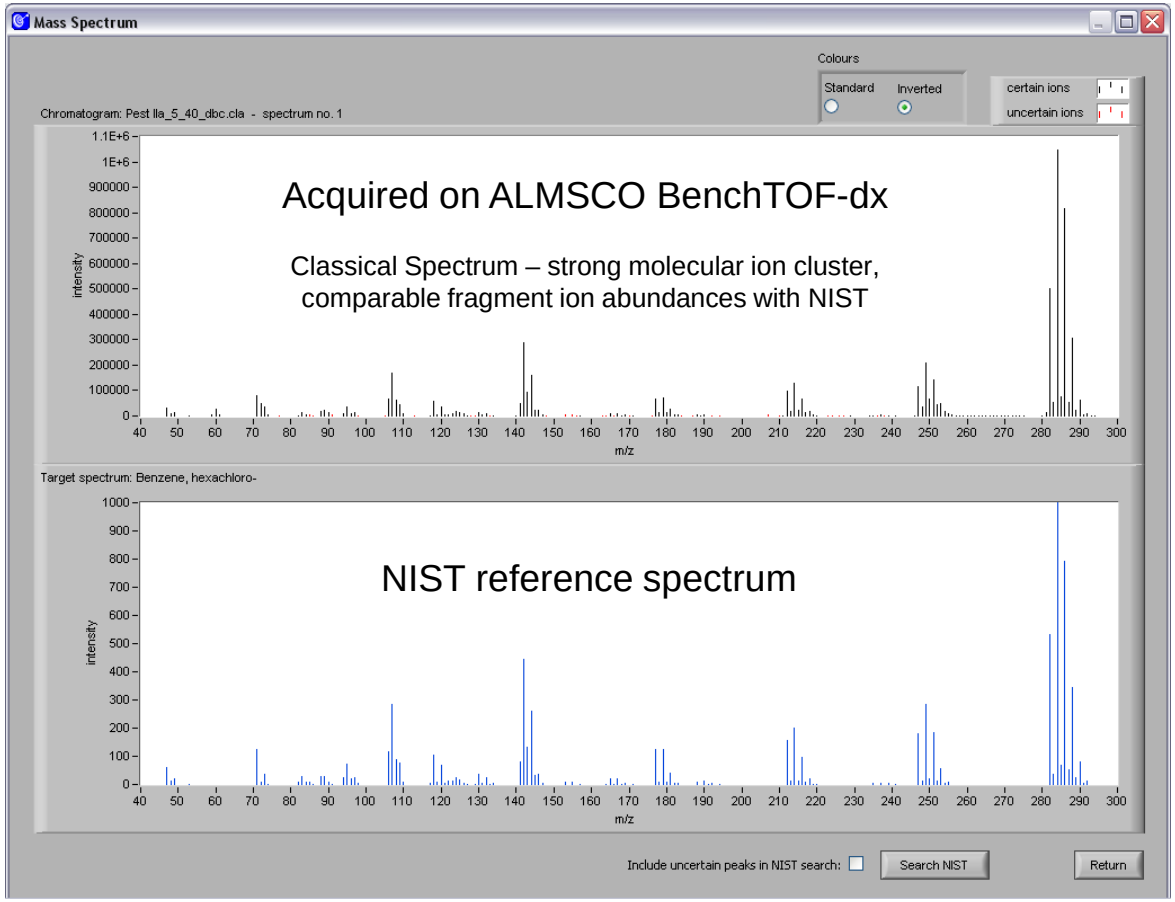


Presented at Pittsburgh Conference 2003.; “Fast Screening for Pesticides in Food by Gas Chromatography – Time-of-Flight Mass Spectrometry”.

www.markes.com

Today,
a new standard in GC/TOF spectral fidelity

HCB spectrum from an extract of hops



Data courtesy of Prof H Nitz, Department of Brewing Technology and Quality, Weihenstephan, Technical University Munich

MARKES international

www.markes.com

What does BenchTOF-dx offer?

- Spectral Accuracy
- Sensitivity
- Clarity
- Selectivity

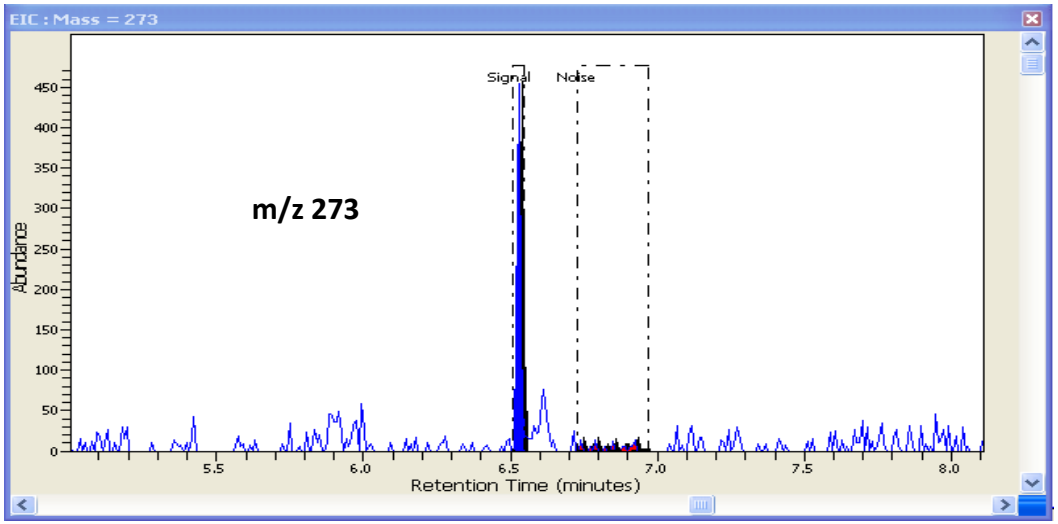
Sensitivity

- A quadrupole analyser is a mass filter
  - Scanning is extremely wasteful of ions formed in the source
- Quad analyser duty cycle is very low in scan mode
  - < 0.5% for scanning 45-250 amu (VOCs)
  - < 0.2% for scanning 45-500 amu (SVOCs)
  - < 0.1% for high mass applications (e.g. PBDEs)
- A TOF analyser does not filter
  - >90% ions injected into analyser can be detected
  - This is Comprehensive MS, not Wasteful MS

Sensitivity

- S/N values 800:1 for 1pg OFN from full range spectra (1-1000 amu)
- Enhanced sensitivity is a function of direct (axialzion extraction (c.f oa-TOFs)
- High ionisation efficiency/ transmission rates
- Femtogram-level detection

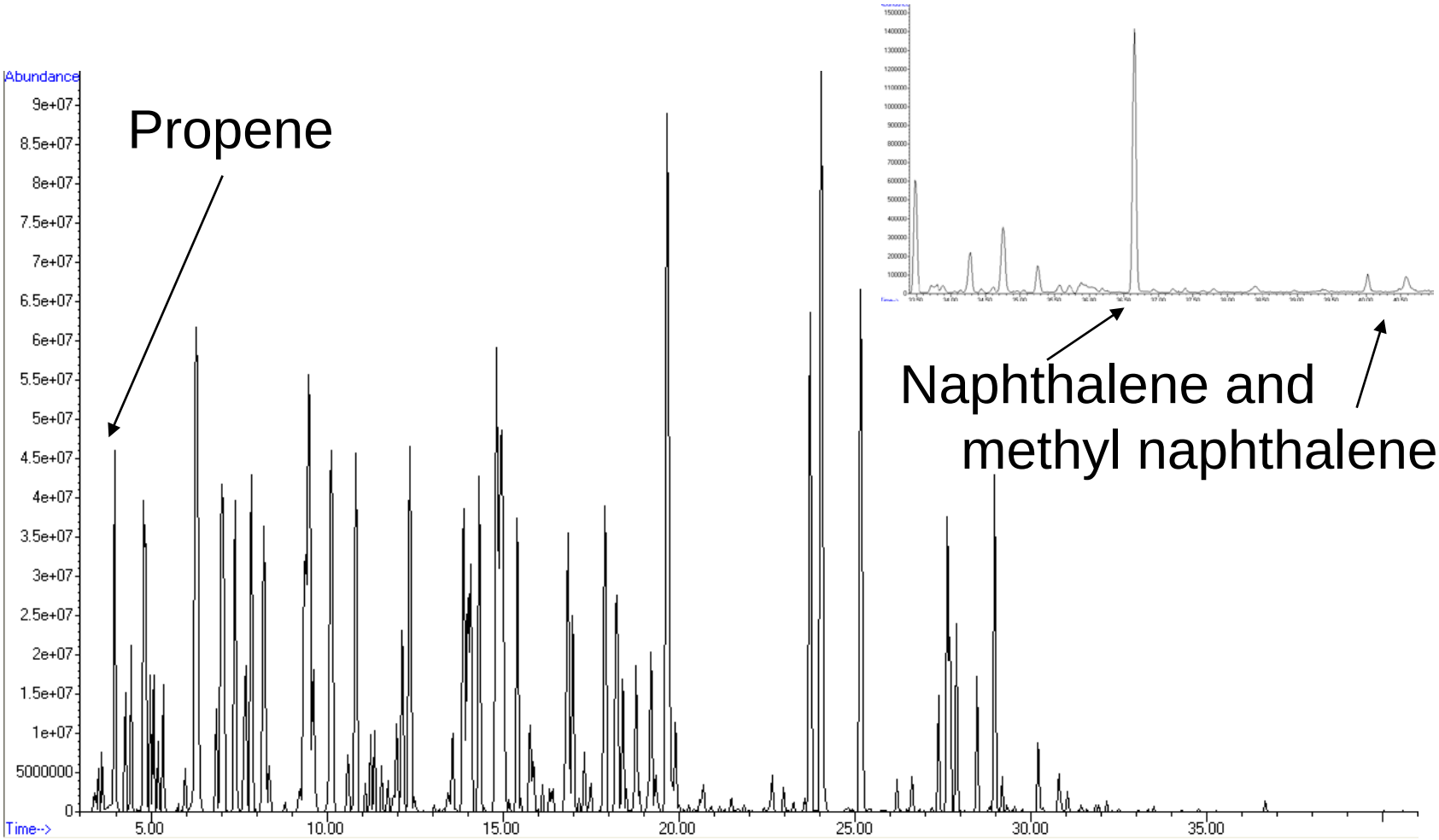
OFN ^{13}C rel ab	~11% ^{12}C
^{12}C OFN	= 1pg,
^{13}C OFN	= 110fg
^{13}C S/N	~108:1
	(MDL ~ 3fg)



OFN ^{13}C isomer S/N (RMS) 80:1

www.markes.com

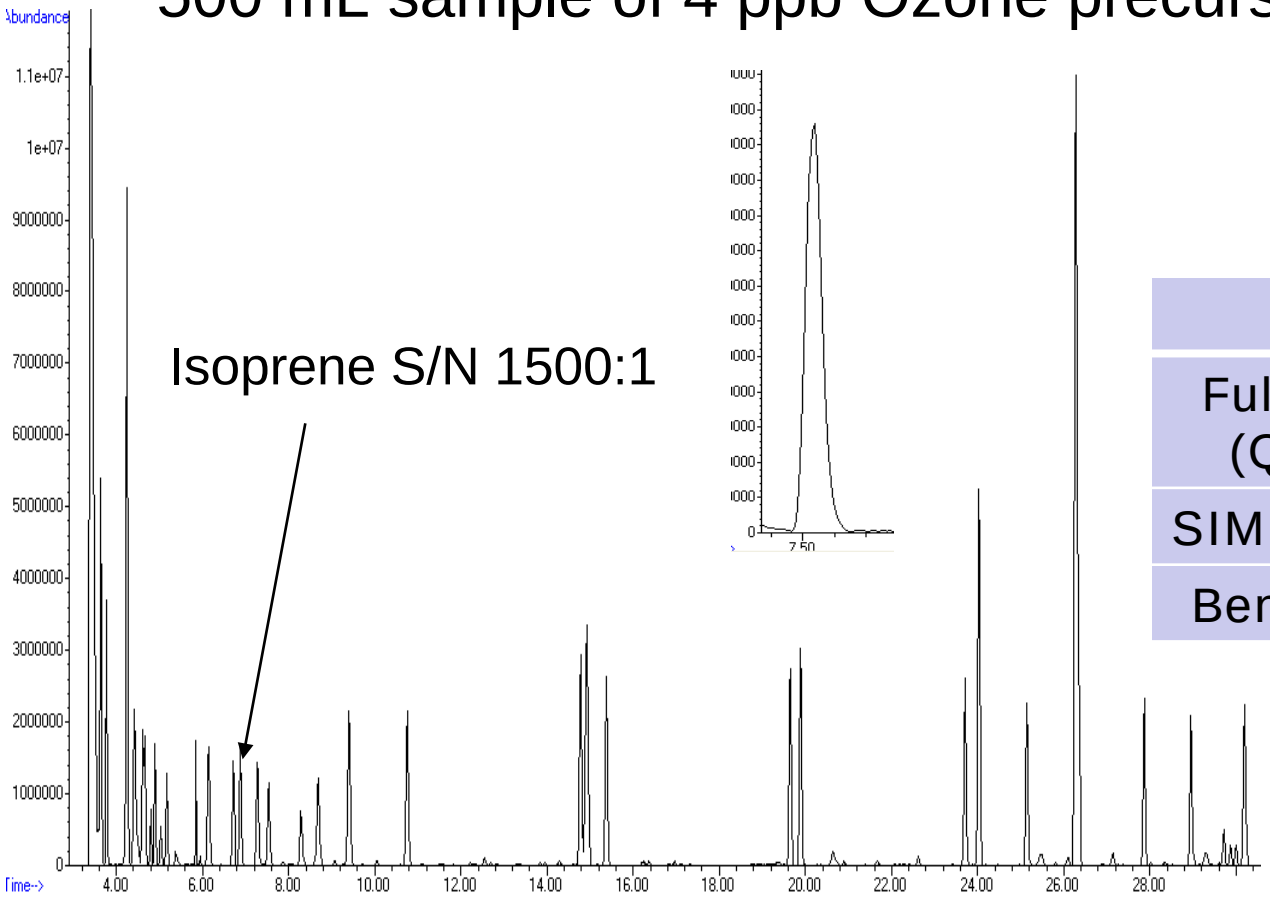
Small sample volumes ideal for Time of Flight



50 mL sample volume near diesel car exhaust

Comparison with Quadrupole

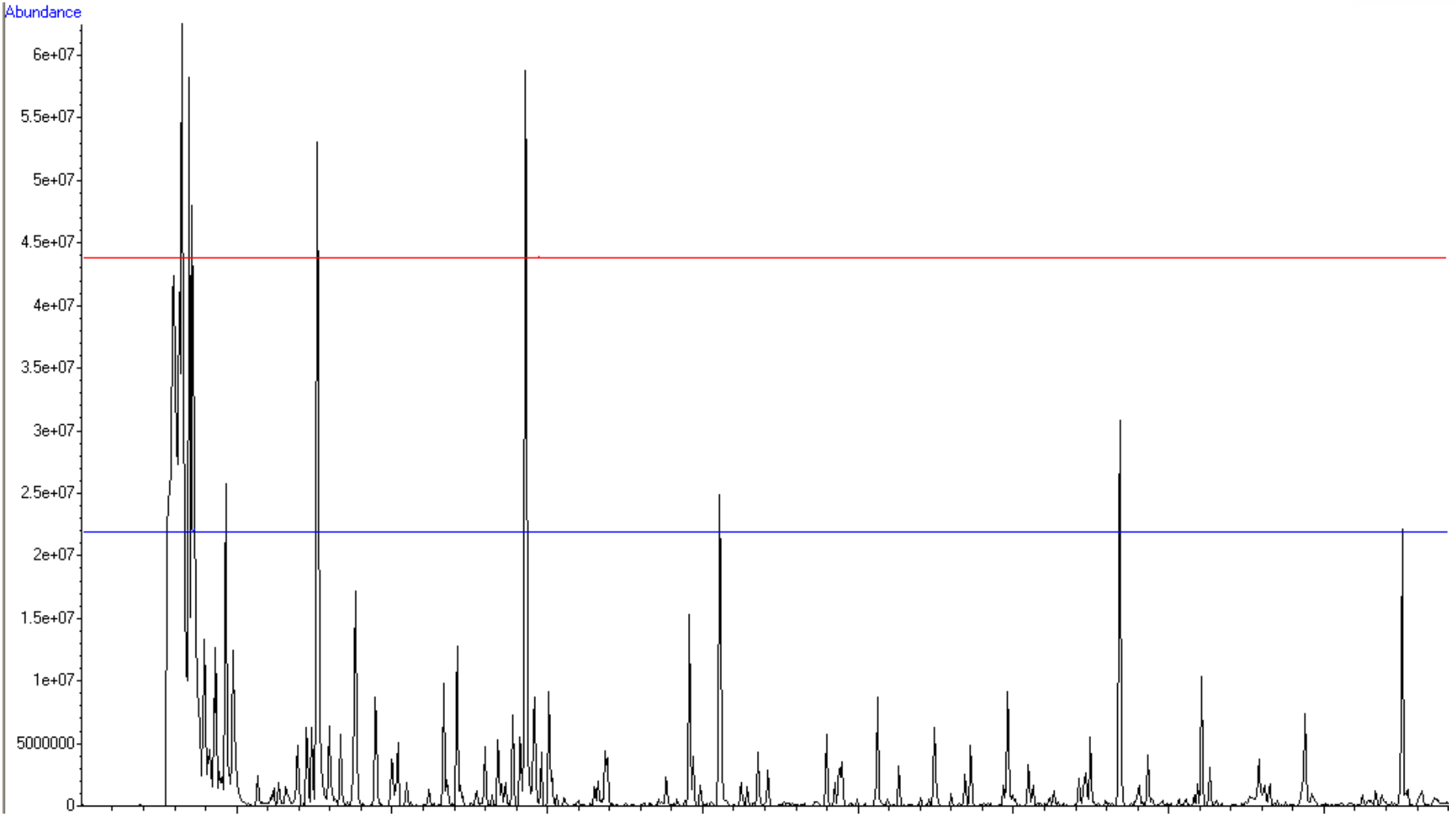
500 mL sample of 4 ppb Ozone precursor standard



	S/N
Full Scan (Quad)	15:1
SIM (Quad)	200:1
BenchTOF	1500:1

www.markes.com

200 mL of ambient rural air

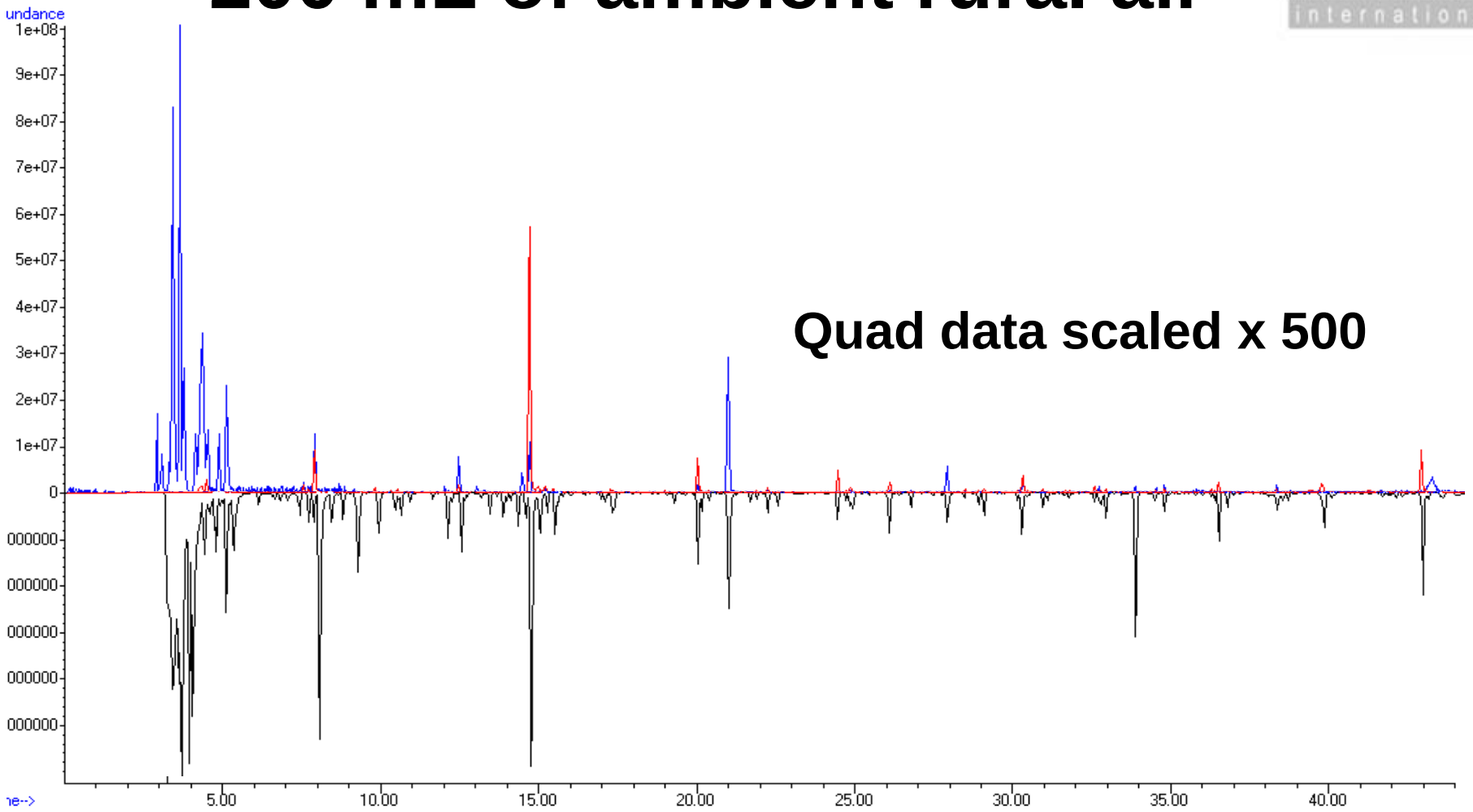


BenchTOF data,
Quad data **Full scan** & **SIM** (ten ions)

MARKES international

www.markes.com

200 mL of ambient rural air



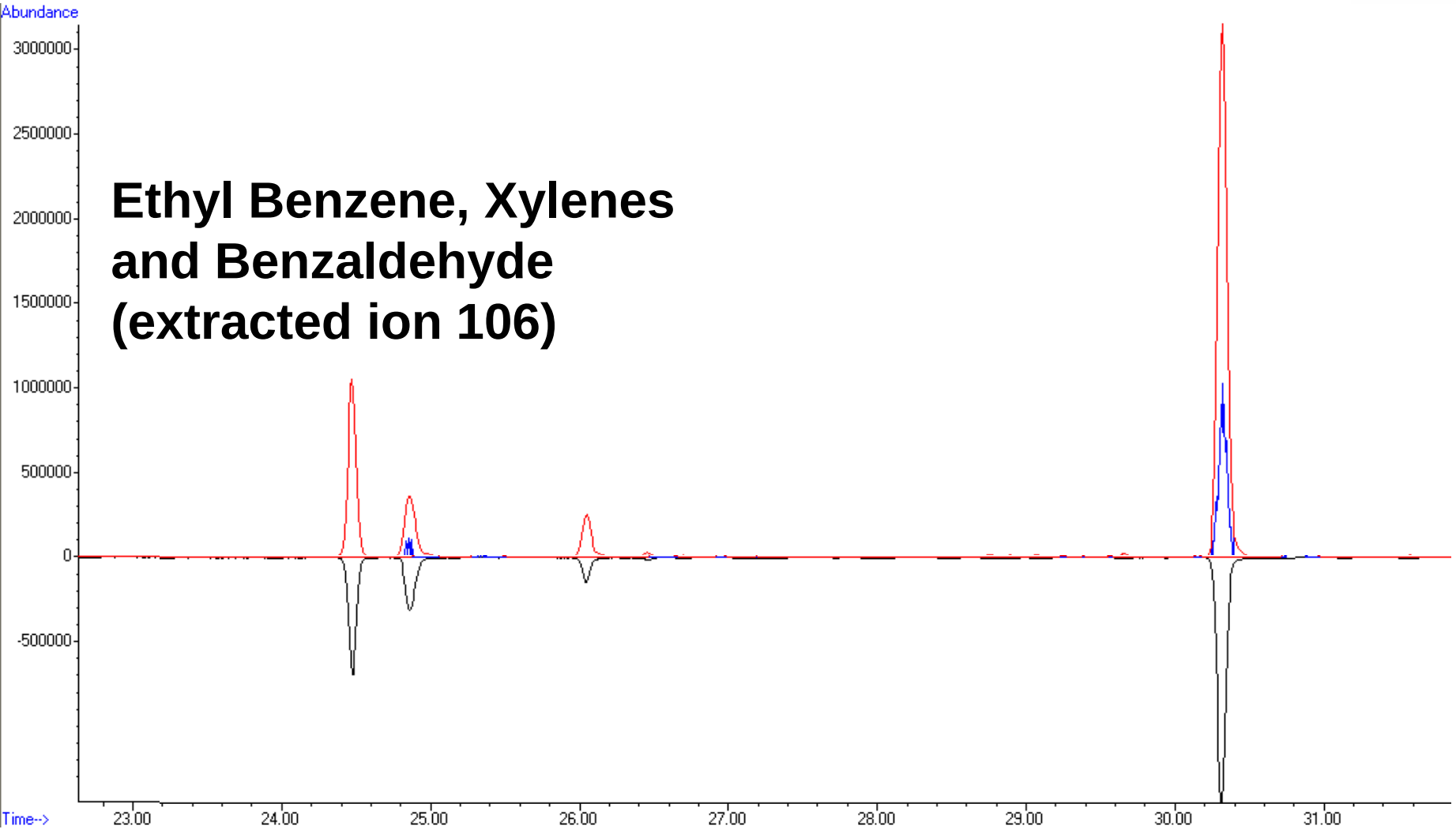
BenchTOF data, Quad data **Full scan** and **SIM** (ten ions)

MARKES international

ALMSCO international

www.markes.com

200 mL of ambient rural air



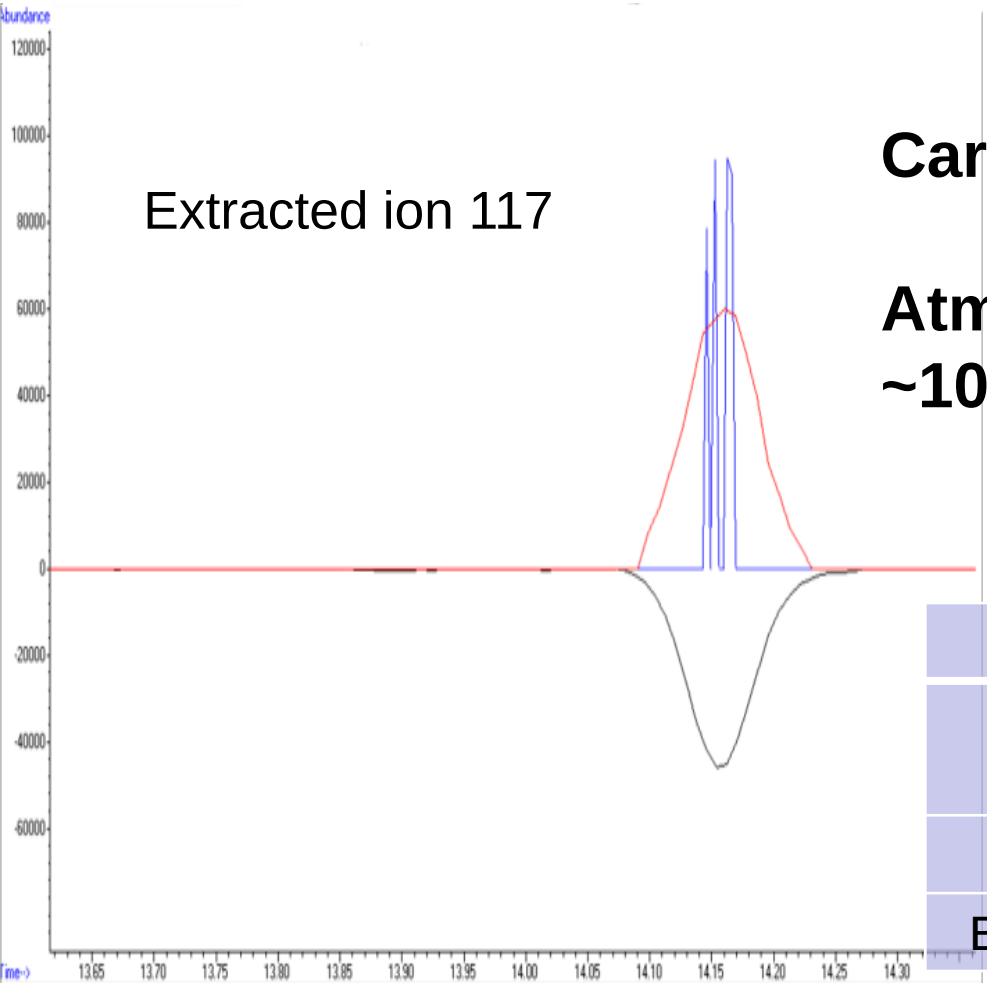
Ethyl Benzene, Xylenes and Benzaldehyde (extracted ion 106)

BenchTOF data,
Quad data(x 500) **Full scan** and **SIM** (ten ions)

MARKES international

www.markes.com

200 mL of ambient rural air



Extracted ion 117

Carbon Tetrachloride

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

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

TOF data,
Quad data(x 500) **Full scan** and **SIM** (ten ions)

www.markes.com

Summary

- Sampling on to sorbent tubes has been simplified
  - No need to worry about
    - Breakthrough
    - Calibration
    - Training operators
- Sample volumes between 50 ml and 500 mL can be taken to deal with high and low concentration samples
- High humidity environments – take small sample volumes; less water sampled
- Combined with BenchTOF-dx provides SIM or better LOD's but with full spectral information.

MARKES international

Any Questions?

MARKES international

www.markes.com