Centri Applications

Exploring new areas and improving analytical quality of volatiles and semi-volatiles analysis

MARKES international

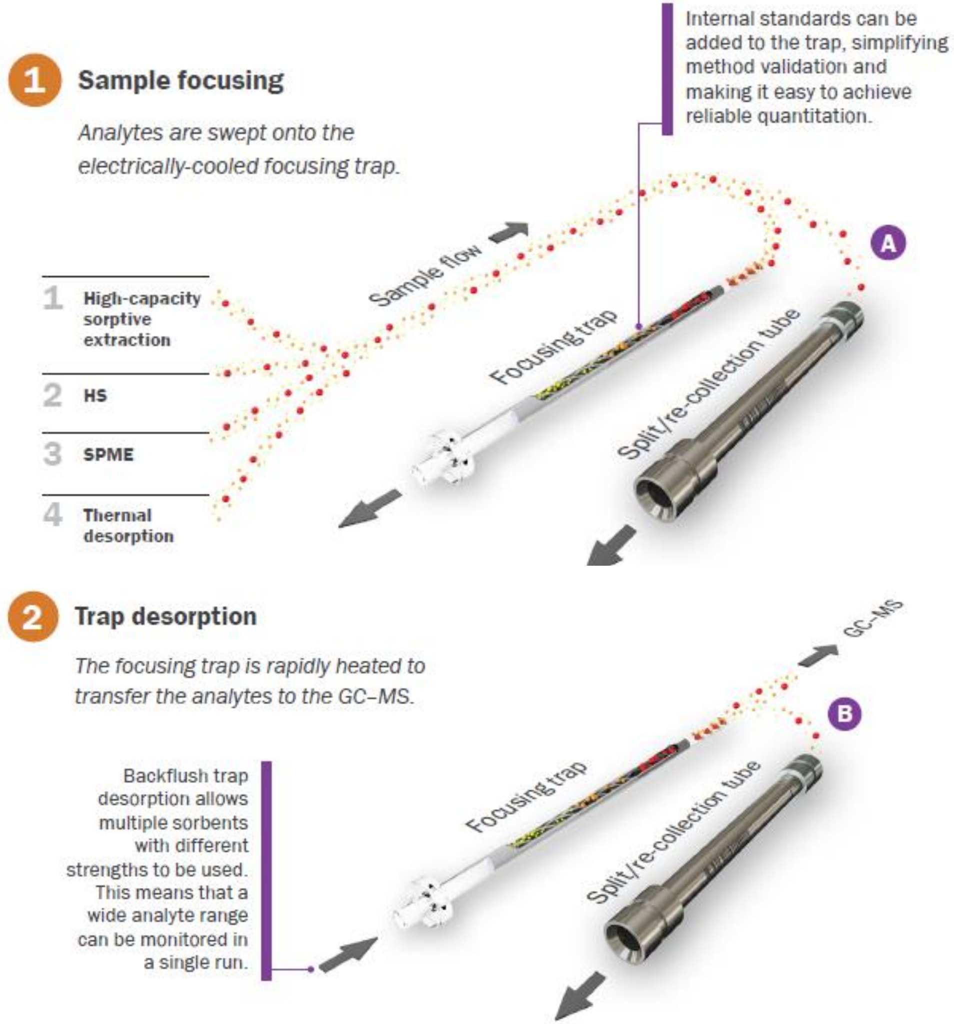
Ingeniería Analítica Chromatography & Spectrometry

THE QUEEN'S AWARDS FOR ENTERPRISE: INTERNATIONAL TRADE 2015

Advantages of using a focusing trap for preconcentration

Enhanced performance with cold trap refocussing

HS-trap, SPME-trap, HiSorb probe-trap, TD-trap..

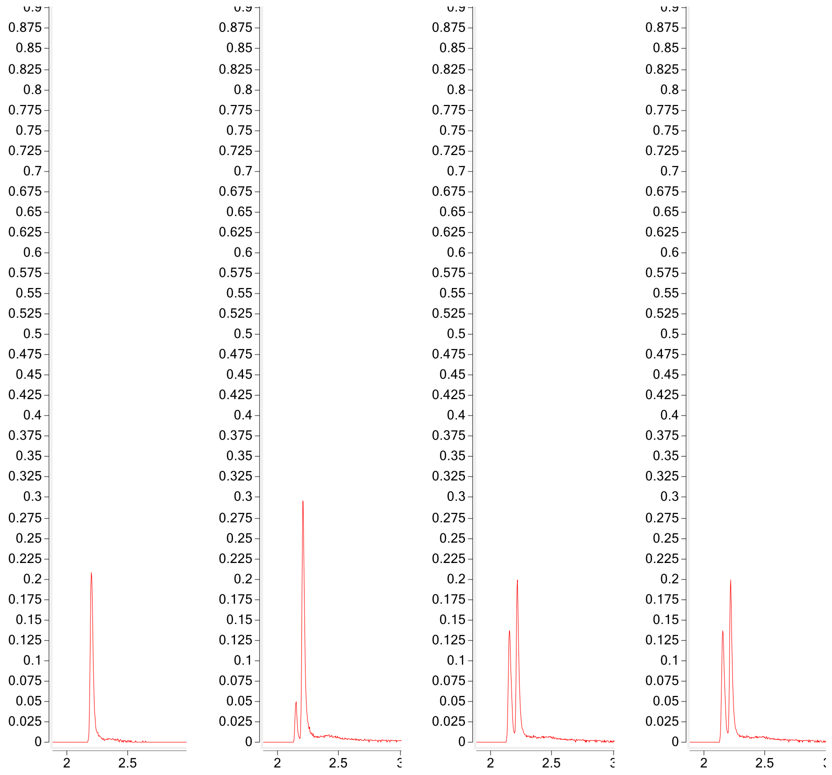


- Preconcentration = Improved peak shape = enhanced S/N = Gain in sensitivity
- Hydrophobic sorbents and trap purge parameters for water and solvent management
- Multi bed sorbents for selective refocussing across extended volatility range
- Peltier cooled sub-ambient trap control providing maximum trapping efficiency
- Automated re-collection (TD-50) in all sampling modes- HiLo analysis, unique SPME, Probe, HS operation

HS-Trap vs. Direct HS

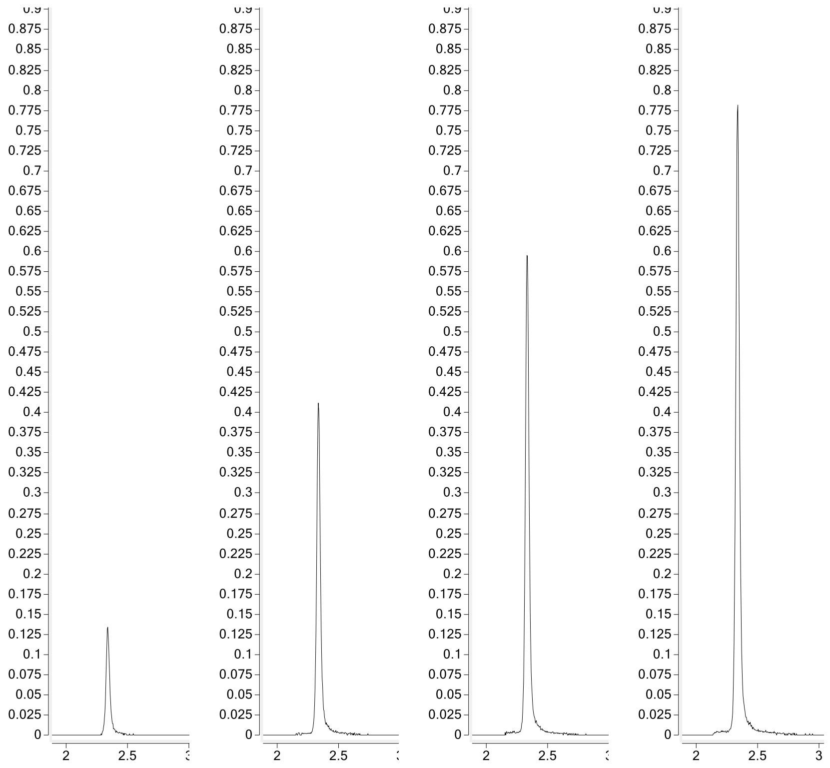
Effect of injection volume on peak shape

Direct HS



0.5mL 1.5mL 2.0mL 2.5mL

HS-Trap



0.5mL 1.5mL 2.0mL 2.5mL

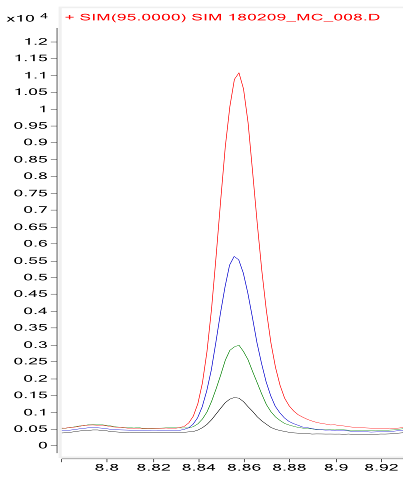
Centri: Headspace-trap

Effect of injection volume on peak shape

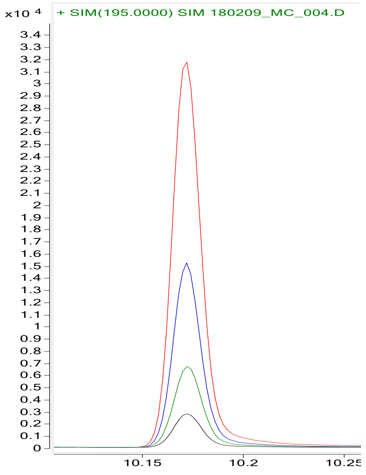
Trap Critical

- Headspace Analysis- Sample: 10mL @500ppt odourants in water
- Increasing the HS sample volume by a factor of 10
- No loss in peak shape/symmetry across this range
- No peak splitting observed at higher volume
- Incremental gain in sensitivity
- *Splitless analysis*

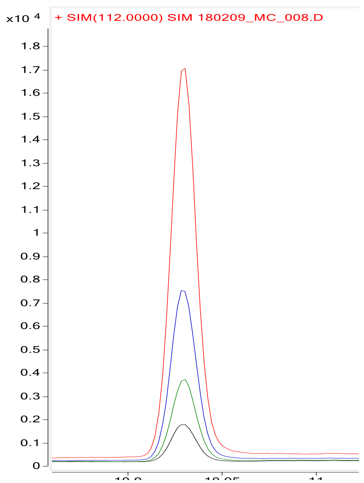
Inj. Vol.
0.5mL
1mL
2mL
5mL



2-MIB



2,4,6-TCA



Geosmin

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Volatile organic compounds in drinking water

Water

A fundamental resource for life

- Water is one of the most precious resources we have, and it needs protecting and safeguarding
- More than one-quarter of all bottled water comes from a municipal water supply – the same place that tap water comes from
- The access to safe drinking-water is essential to health, a basic human right and a component of effective policy for health protection (WHO Guidelines 2008)
- A two-person household (UK) uses ~100,000 L per year (92.5% goes to waste)

Drinking water

Environmental water

Waste water

Ground water

Water comes in multiple types

VOCs in drinking water

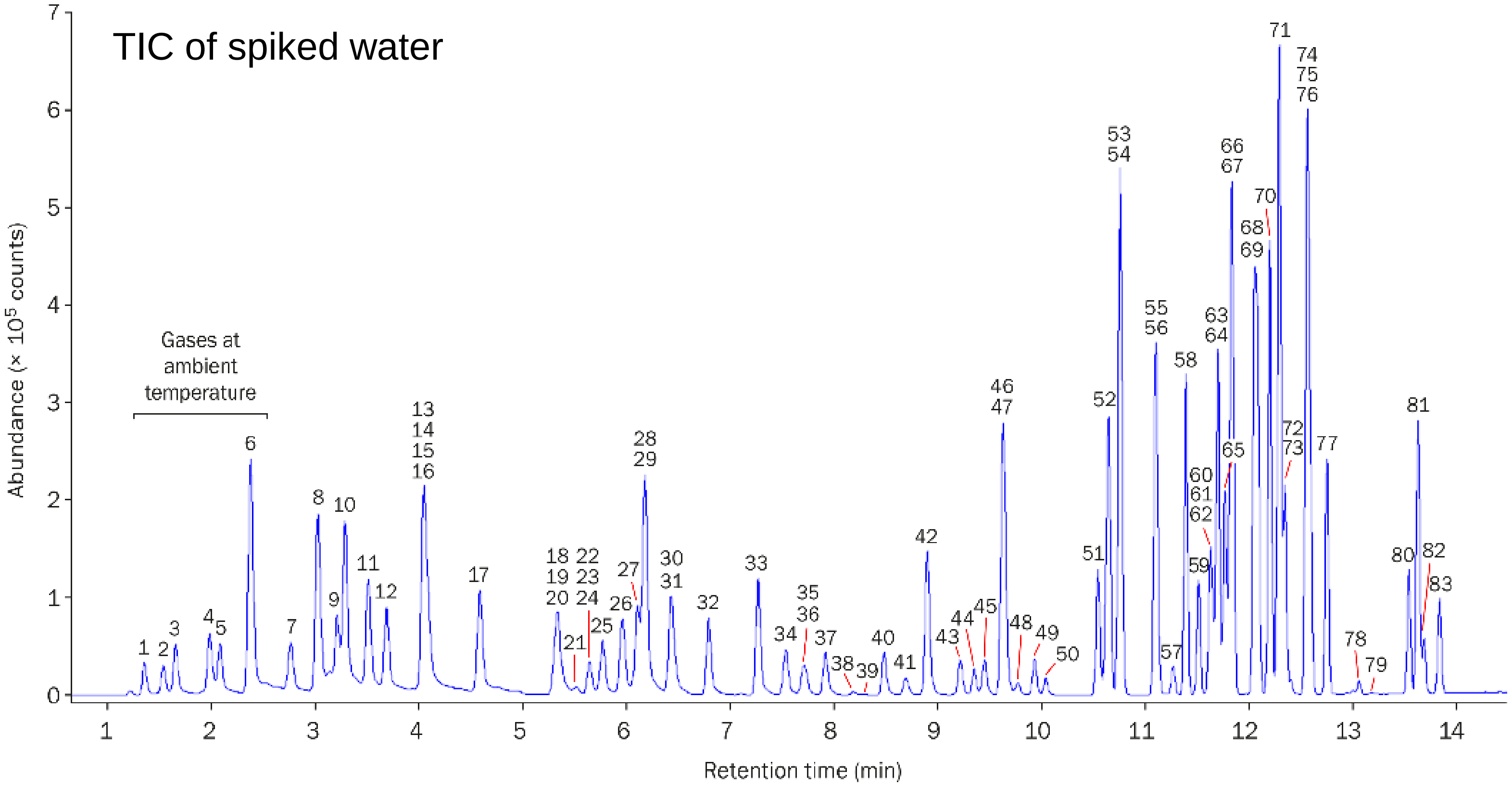
Maximum/reporting levels for example contaminants

Compound	US EPA	China EPA	European EEA	Canadian CDWQG	WHO guidelines
Benzene	5 ppb	10 ppb (0.01 mg/L)	1 ppb (0.001 mg/L)	5 ppb (5 µg/L)	10 ppb
Ethylbenzene	700 ppb	300 ppb (0.3mg/L)	—	140 ppb (140 µg/L)	300 ppb
Benzo[a]pyrene	0.2 ppb	0.01 ppb (0.00001 mg/L)	0.01 ppb (0.00001 mg/L)	0.04 ppb (0.04 µg/L)	All PAHs: 0.7 ppb
Xylenes	10 ppm	500 ppb (0.5 mg/L)	—	90 ppb (90 µg/L)	500 ppb
Vinyl chloride	2 ppb	5 ppb (0.005 mg/L)	0.5 ppb (0.0005 mg/L)	2 ppb (2 µg/L)	—

VOCs in drinking water

Headspace–trap analysis

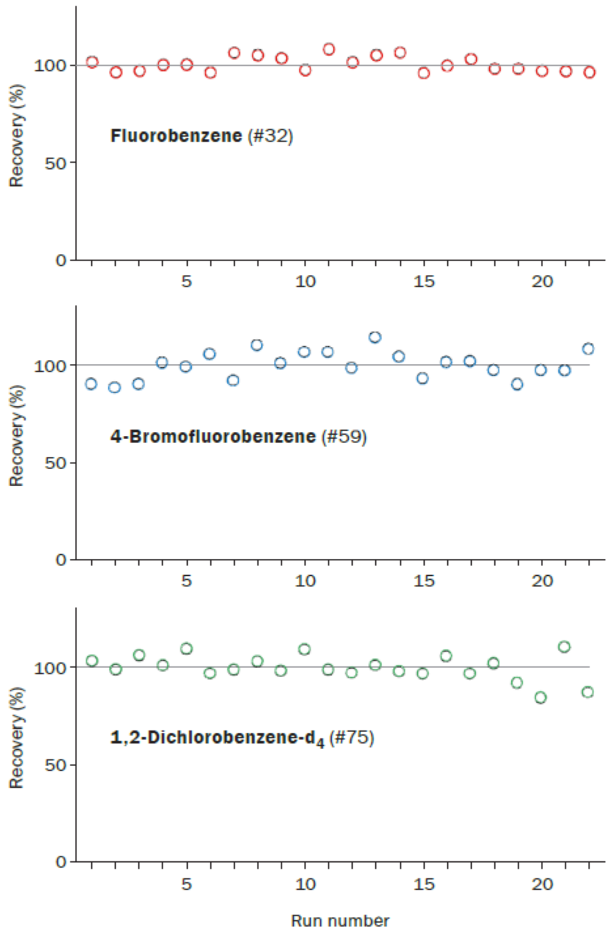
- With BFB tuning
- Minimum detection limits (0.002–0.27 ppb)
- Much lower than reporting limits for:
  - US (0.5 ppb)
  - EU (0.1–100 ppb)
  - China (2–60 ppb)



Application Note 253

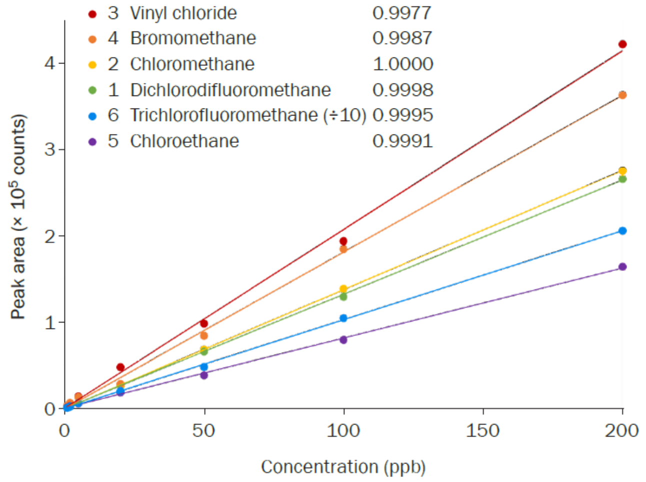
VOCs in drinking water

Reproducibility and linearity

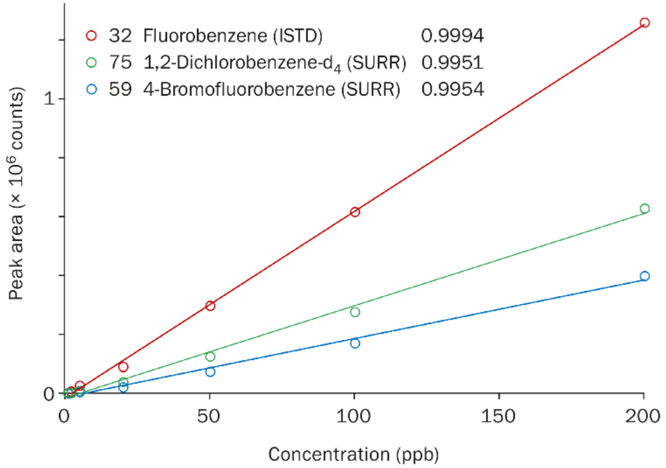


The recoveries for the internal standard and the two surrogates (from 22 consecutive analyses of the 25 ppb standard) fall within the 80–120% range, with RSDs below 10%.

Seven-point calibration curves and R^2 values for the six most volatile compounds



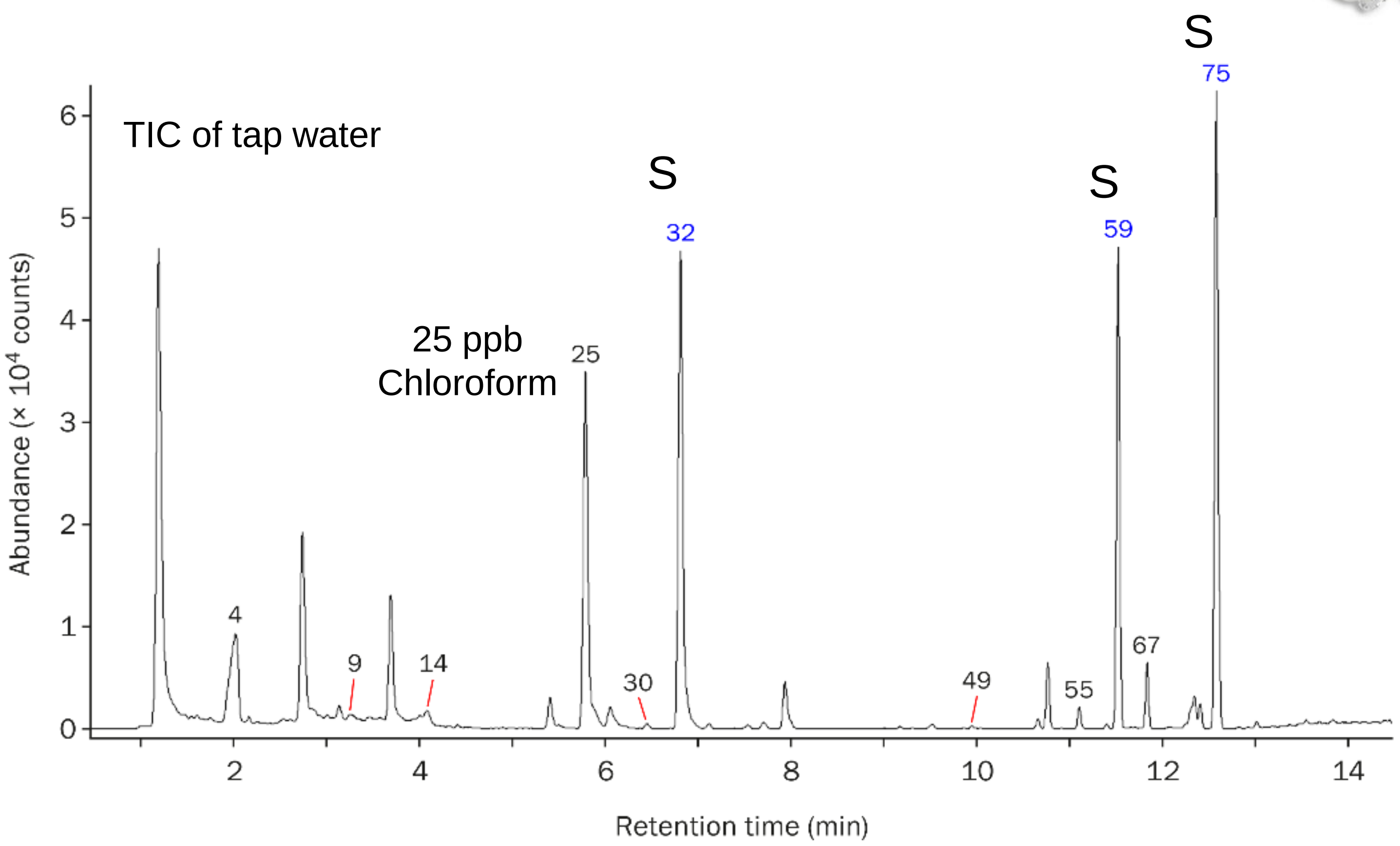
Seven-point calibration curves and R^2 values for the internal standard and the two surrogates



VOCs in drinking water

Welsh drinking water

- Real-world sample of tap water
- Surrogates added at 25 ppb
- 82 compounds <2 ppb
- Exception of chloroform (25 ppb)



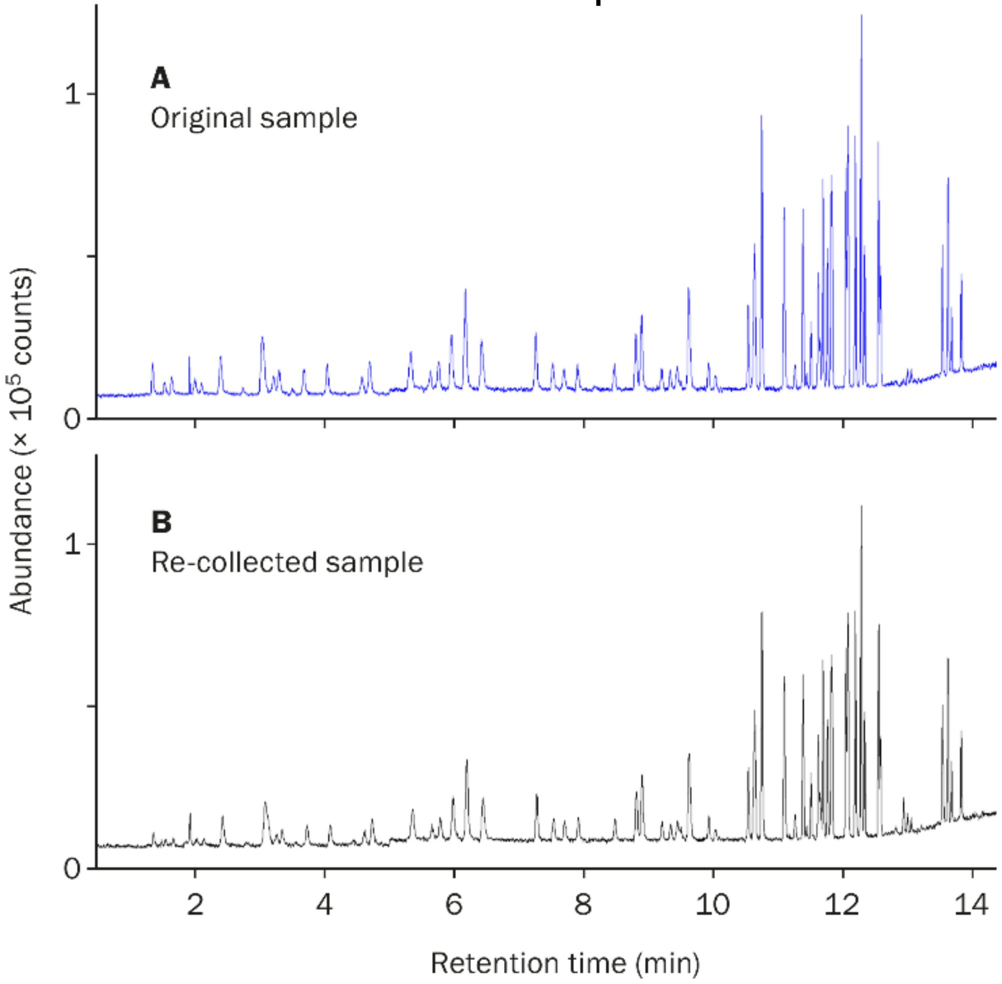
Application Note 253

VOCs in drinking water

Reproducibility – Re-collection

- Repeat analysis without lengthy sample preparation
- Different split conditions possible (‘High–Low’ analysis)
- Protecting the GC column and MS
- Sample security
- Storing samples for later analysis or re-analysis

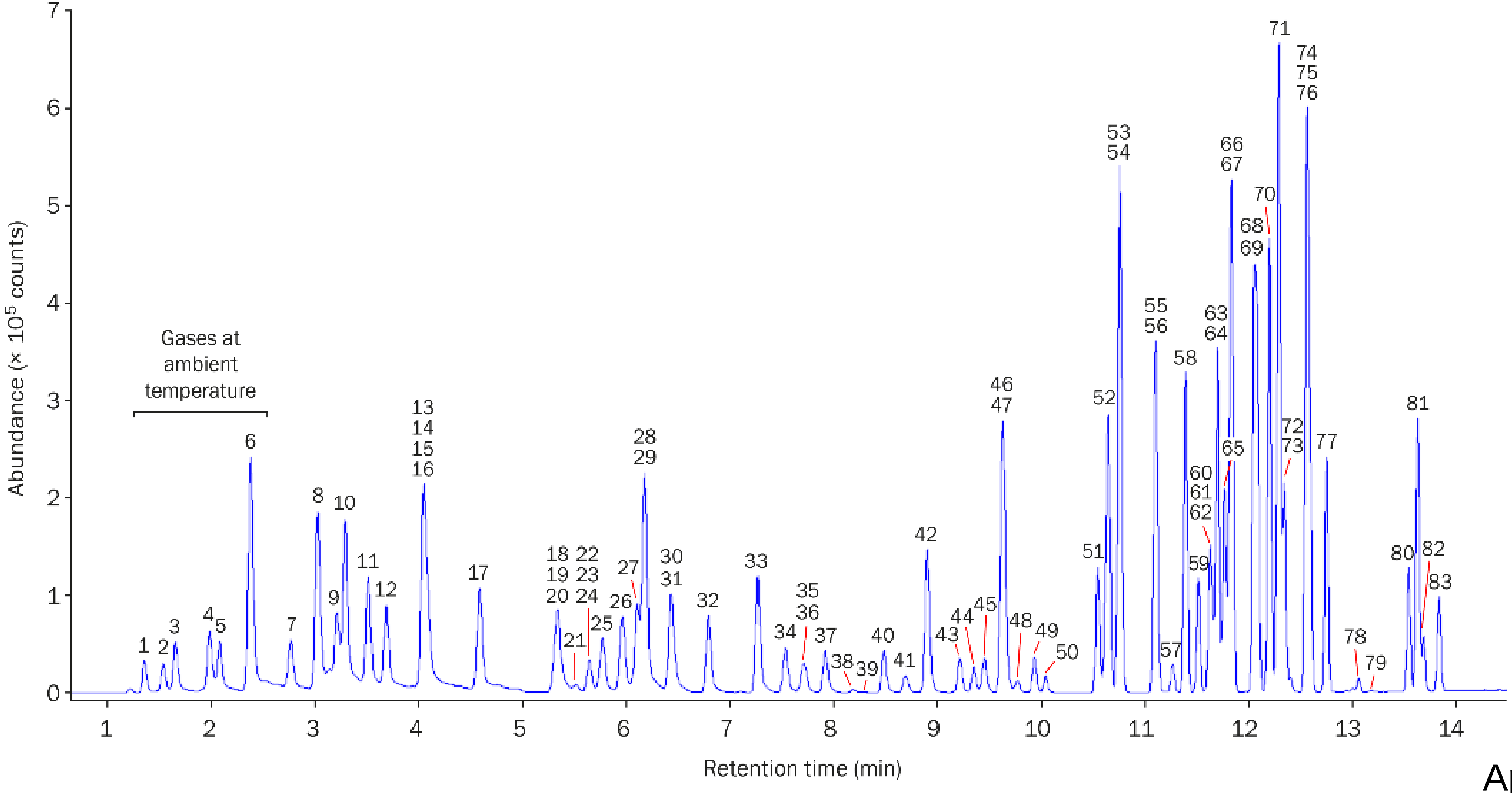
EPA 524.2 compounds



Lowering detection limits of volatiles in water

VOCs in drinking water

Headspace–trap analysis



TIC of spiked water

Application Note 253

Lowering detection limits

..stepping down the ladder

Compounds of interest

Appnote 253

Use Headspace / with trap

Lowering detection limits

..stepping down the ladder

Compounds of interest

Appnote 253

Mass spectrometer

MS

Use Headspace
/ with trap

Use enhanced tuning
& SIM mode

Lowering detection limits

..stepping down the ladder

Compounds of interest

Use Headspace / with trap

Appnote 253

MS

Use enhanced tuning & SIM mode

Mass spectrometer

Increase injection volume from 1 to 5 ml

Injection volume

Lowering detection limits

..stepping down the ladder

Compounds of interest

Appnote 253

MS

Mass spectrometer

Injection volume

Splitless

Use Headspace
/ with trap

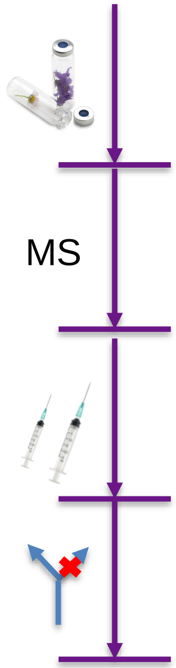
Use enhanced tuning
& SIM mode

Increase injection
volume from 1 to 5 ml

From split to splitless

Lowering detection limits

..stepping down the ladder



Compounds of interest

Appnote 253

Mass spectrometer

Injection volume

Splitless

Use Headspace / with trap

Use enhanced tuning & SIM mode

Increase injection volume from 1 to 5 ml

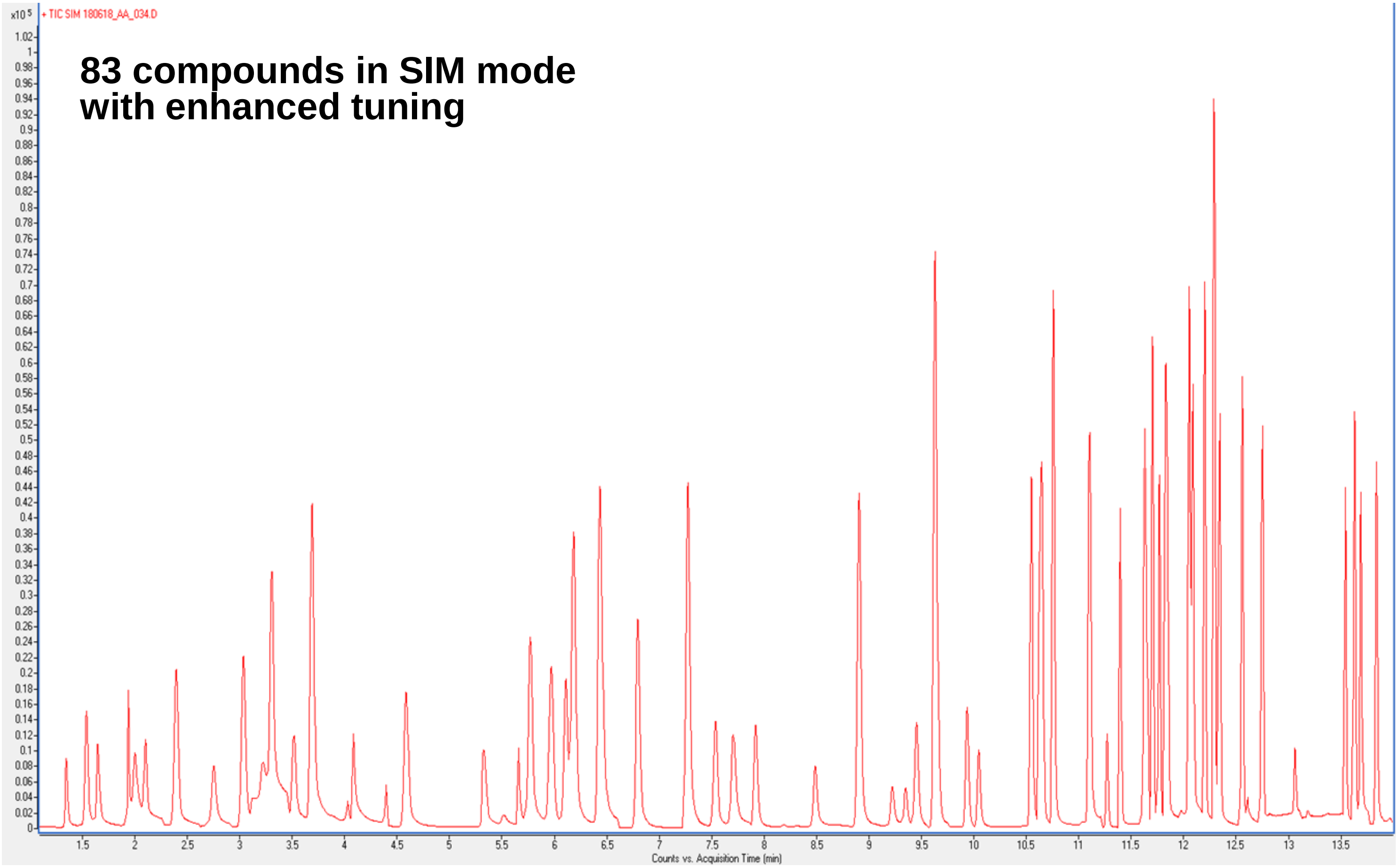
From split to splitless

Why increase sensitivity?

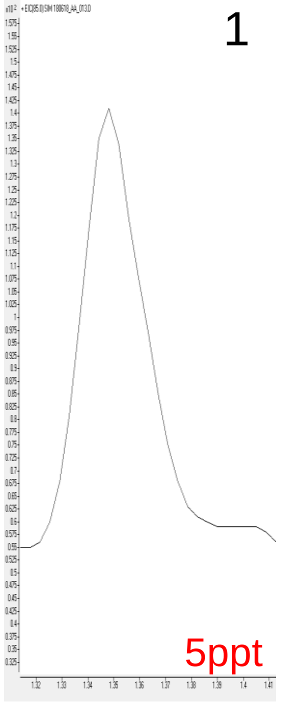
- New insights from heath risks
- Futureproofing
- Being better than the competition
- Meets detection limit across the world.

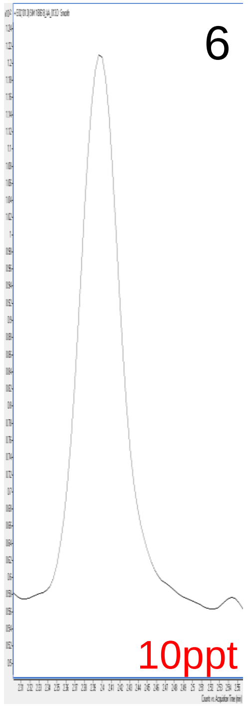
VOCs in drinking water

SIM mode and enhanced tuning



Extracted ion chromatograms for peaks:
#1 (Dichlorodifluoromethane) and
#6 (Trichlorofluoromethane)



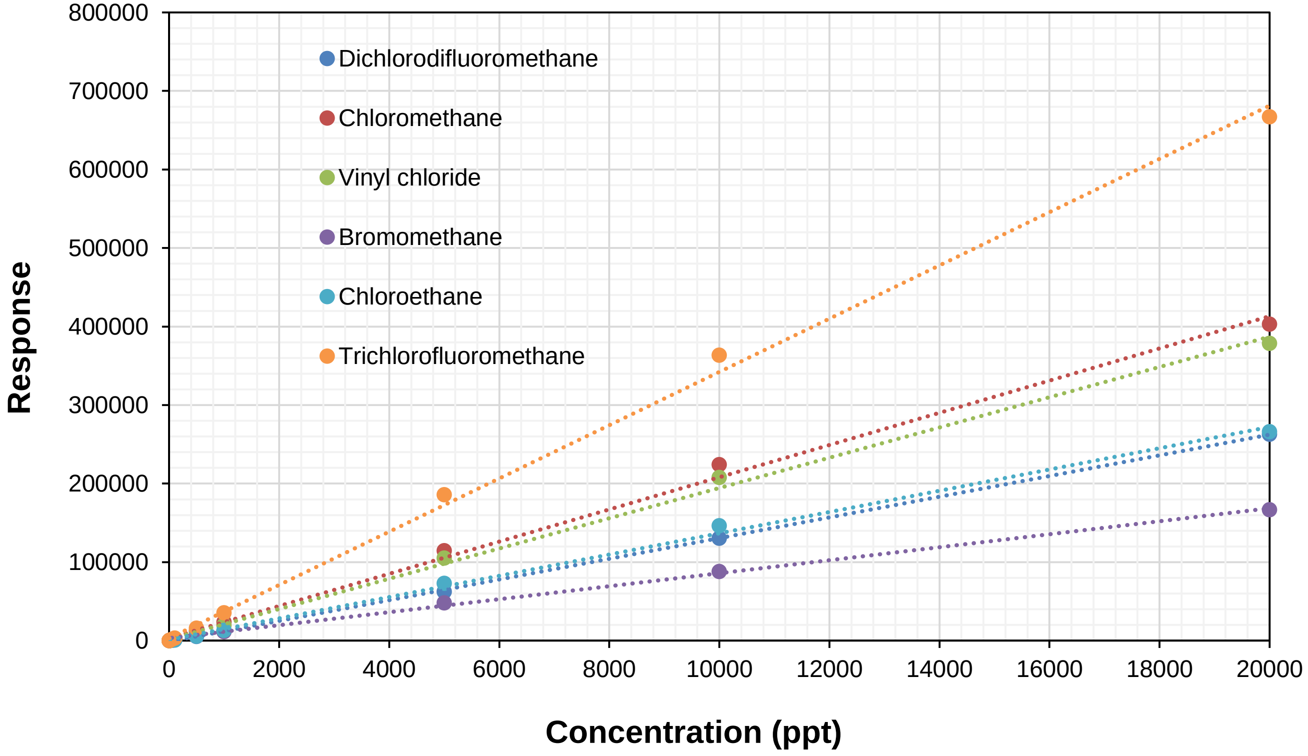


Average MDL: ~3 ppt

VOCs in drinking water

Reproducibility and linearity

- Centri headspace showed excellent linearity and %RSD
- Excellent R^2 all compounds: 0.9980
- Meet the performance required by US EPA 524.2, 8260, HJ810, and 98/83/EC

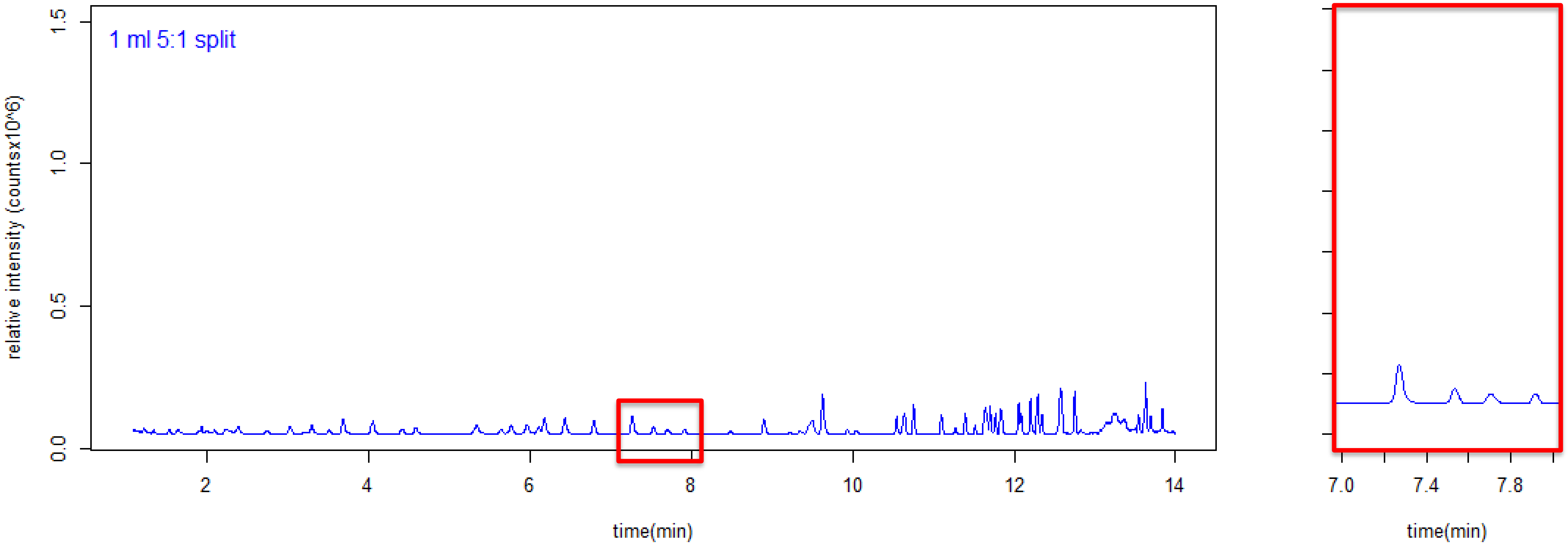


Headspace–trap 1 mL

	Enhanced tuning (SIM mode)
BFB injected	Passed
Calibration & linearity (1 ppt to 20 ppb)	R^2 ~ 0.9980 RRF <14%
Method detection limits	3.32 ppt
Accuracy (5 ppb & 0.5 ppb)	RSD <8%
Precision (5 ppb & 0.5 ppb)	90.10%

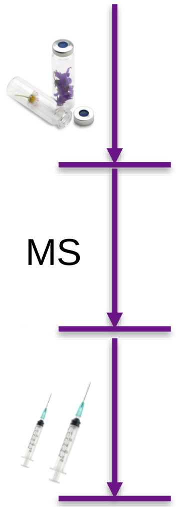
VOCs in drinking water

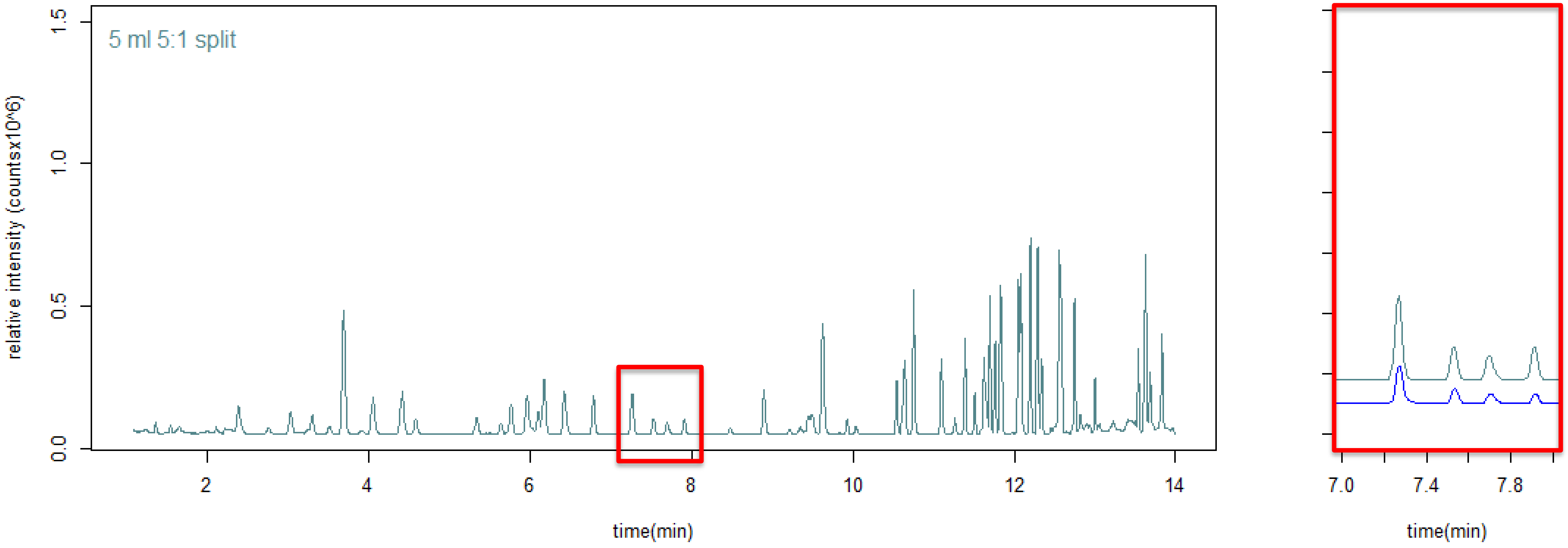
Benefits of adding a cold trap: injection volume



VOCs in drinking water

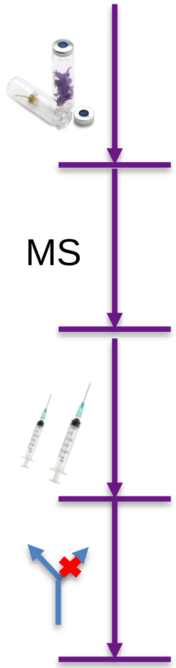
Benefits of adding a cold trap: injection volume

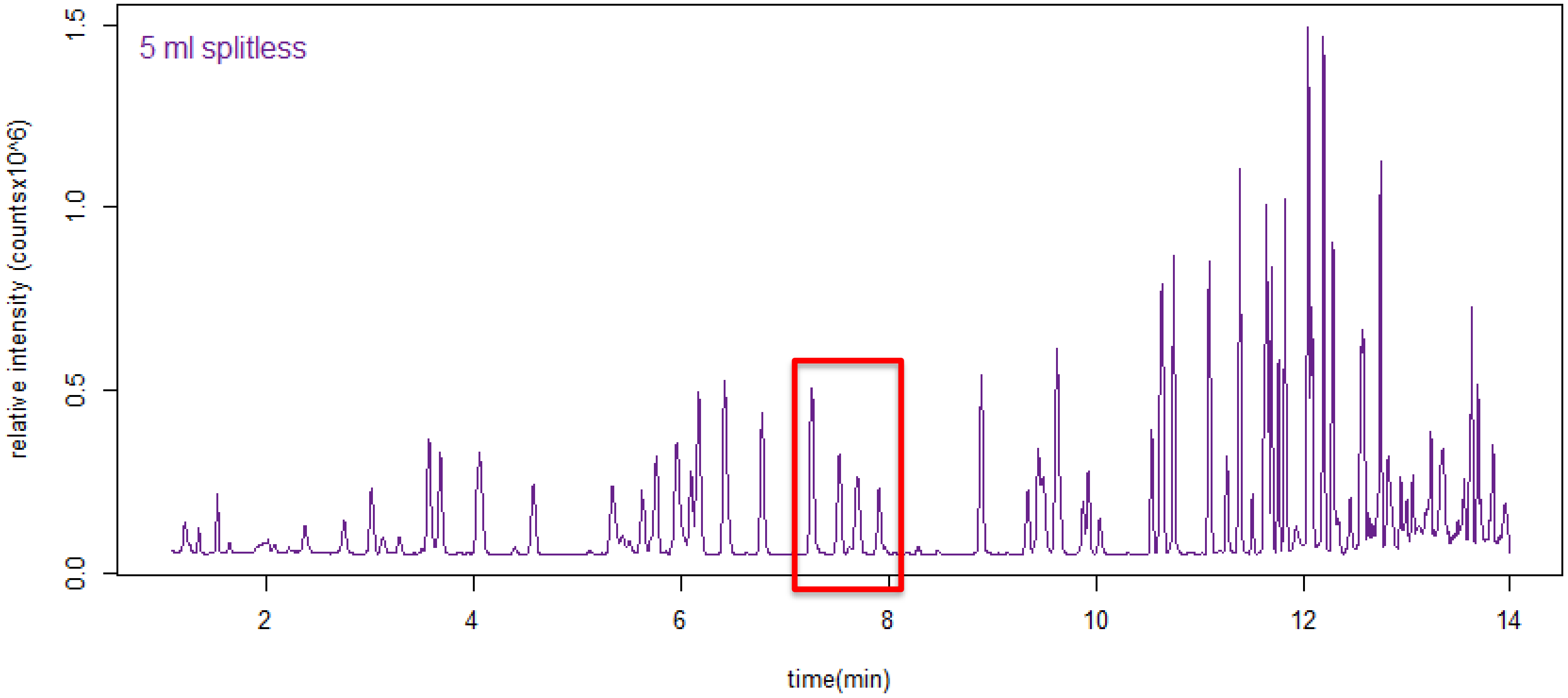


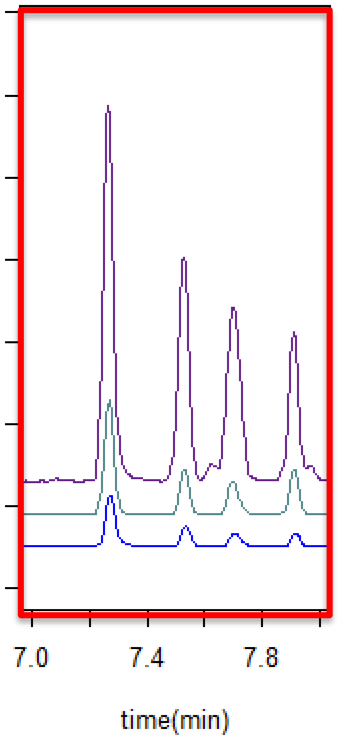


VOCs in drinking water

Benefits of adding a cold trap: splitless injection







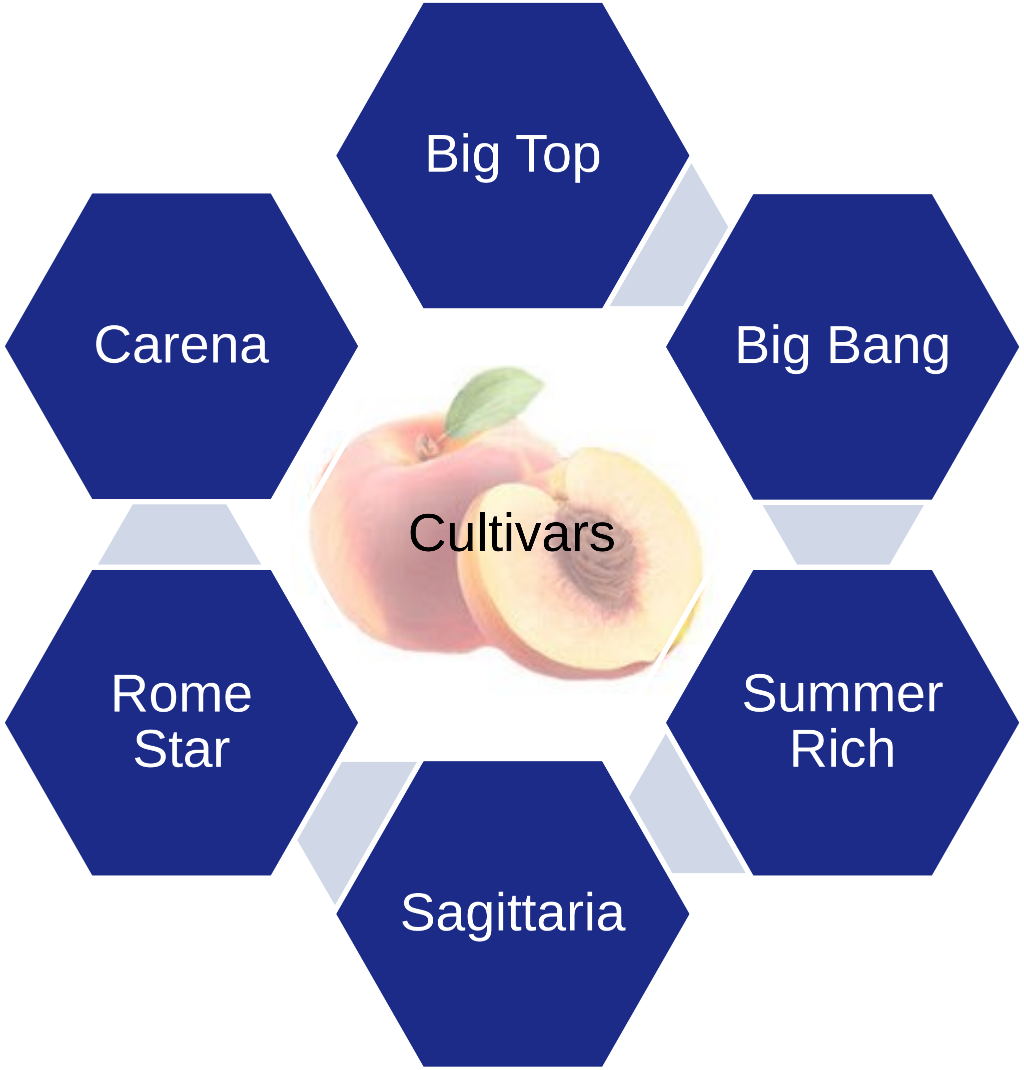
Monitoring fruit quality

A company of the SCHAUENBURG International Group

Monitoring fruit quality

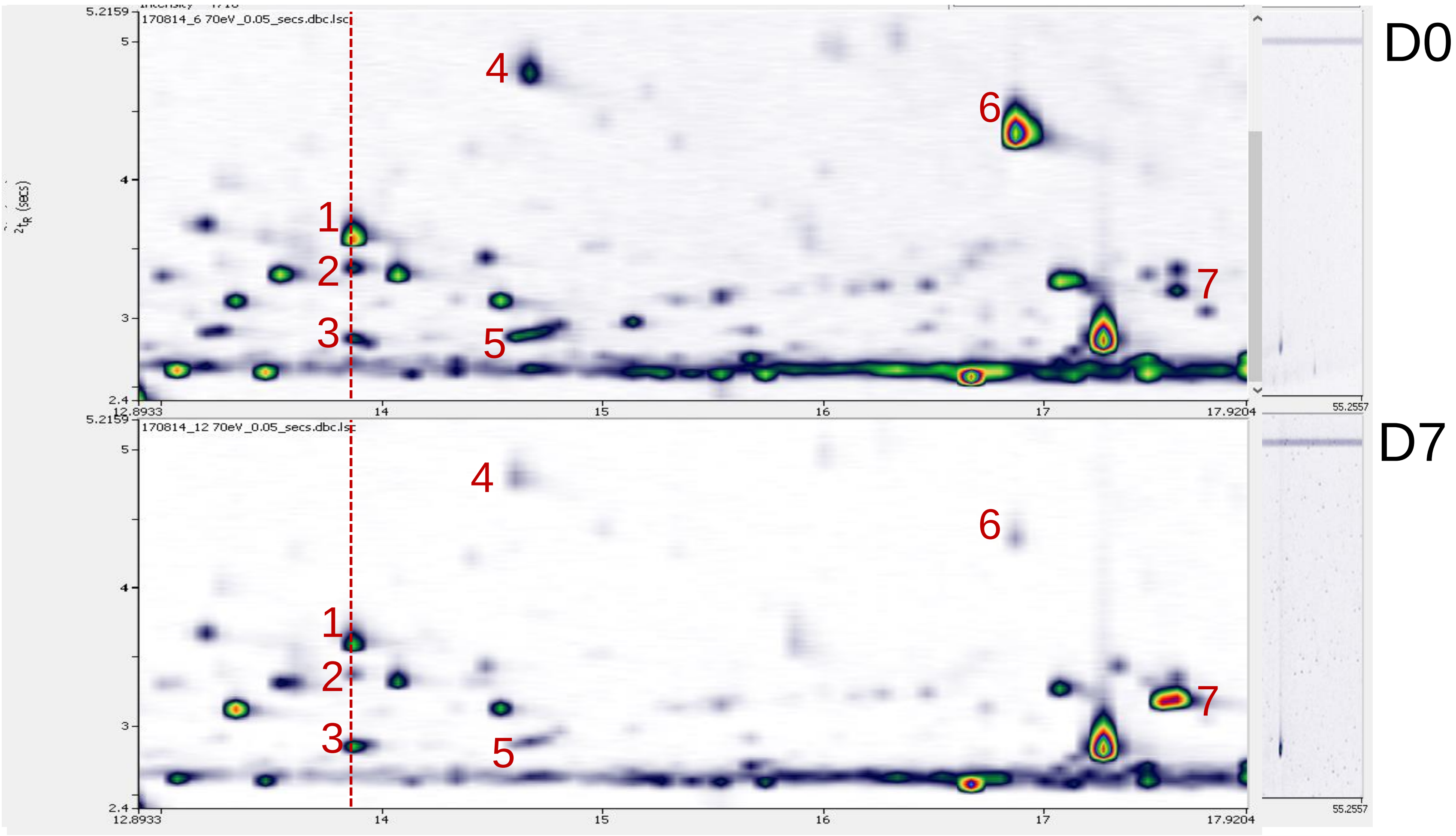
Experiment

- Whole peaches were placed in a roasting bag and left to equilibrate at 20°C for 90 minutes.
- 600 mL of air within the roasting bag drawn directly on to an 'Odour/Sulfur' sorbent tube using an Easy-VOC™ manual pump.
- Sampling at day 0 (D0) and day 7 (D7)
- Empty roasting bags used as control blanks.



Monitoring fruit quality

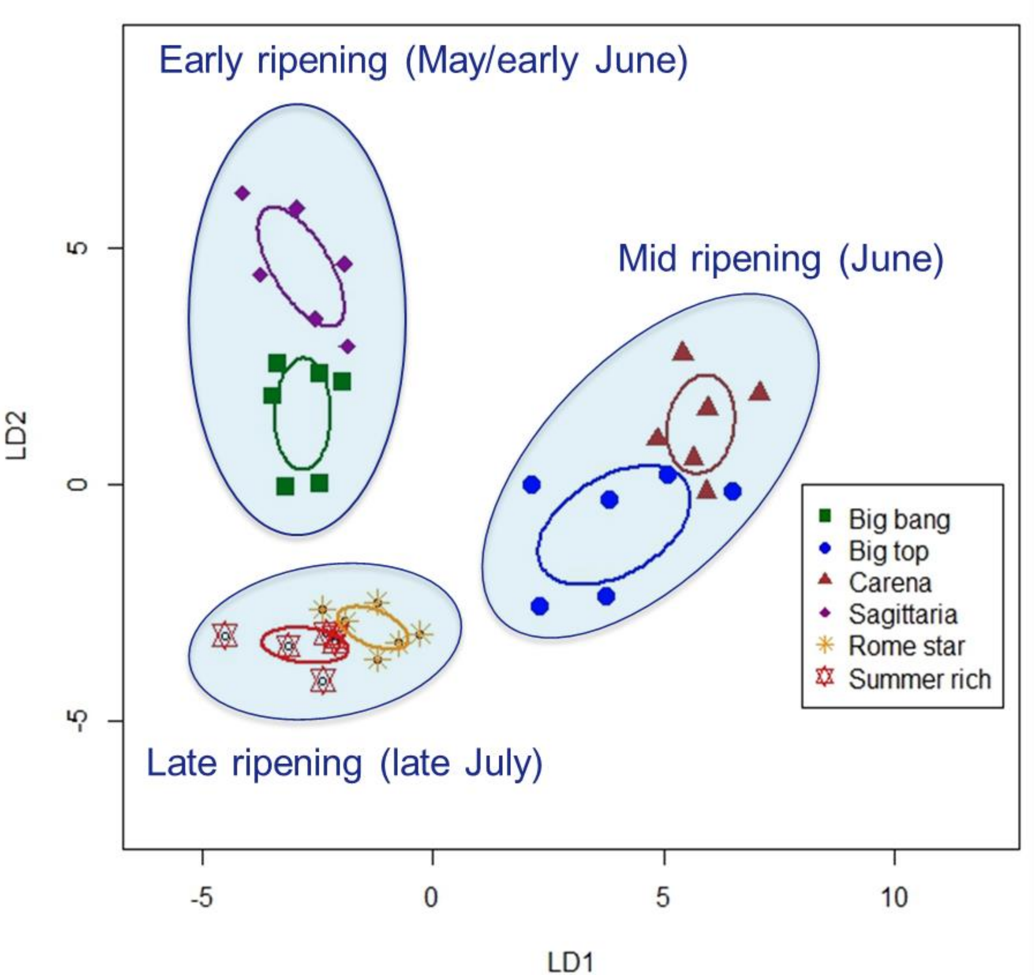
Analysis by Centri-GC×GC-TOF MS



1	*cis*-3-Hexenyl acetate
2	Octanal
3	α-Phellandrene
4	Ethyl hexanol
5	Limonene
6	Linalool
7	Methyl octanoate

Monitoring fruit quality

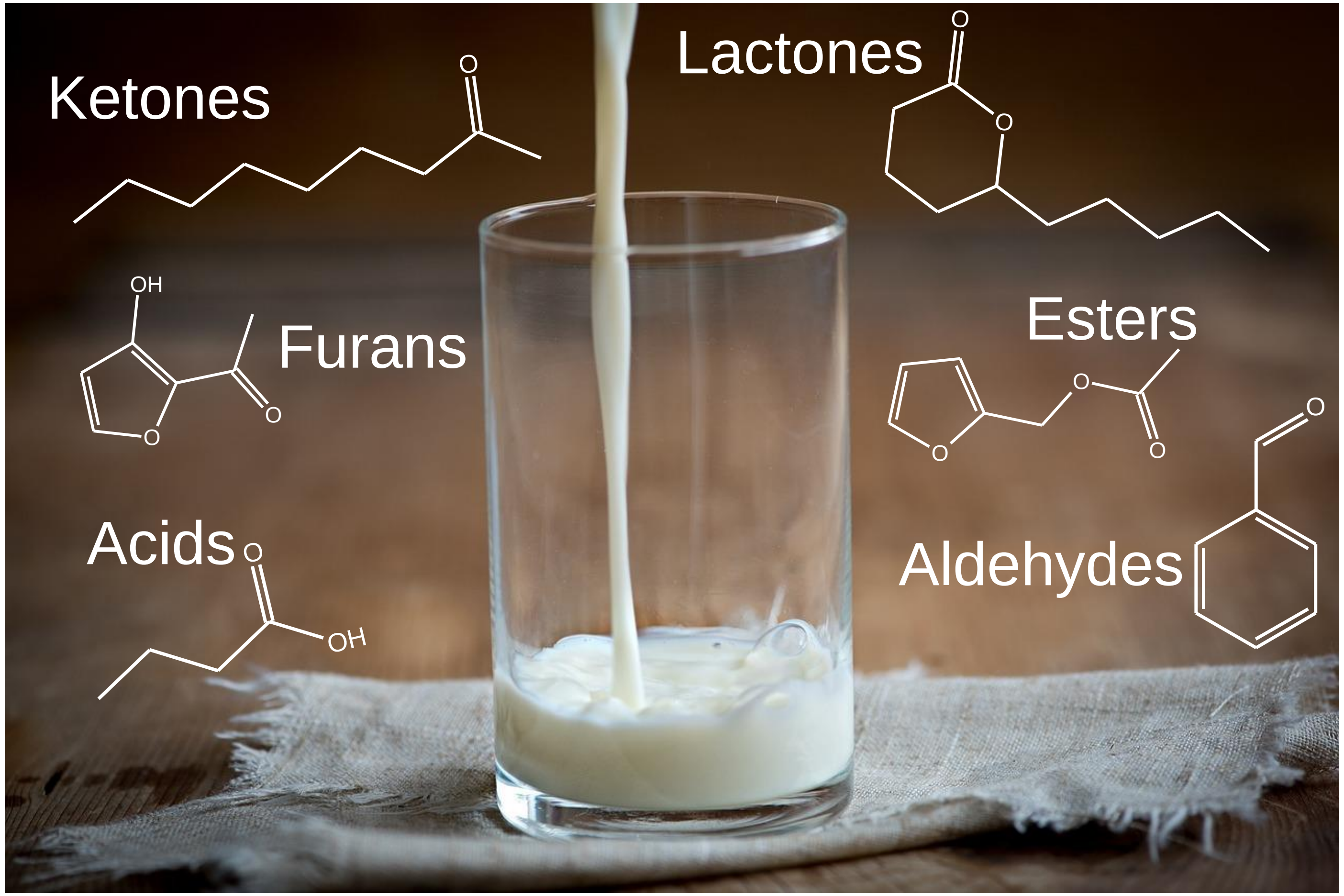
Comparison of aroma profiles



- Statistical analysis of the aroma profiles
- The six cultivars are grouped according to ripening time
- Ethyl octanoate and linalool are major differentiators between the cultivars

Flavour profiling of milk

Milk analysis



Flavour profiling of milk

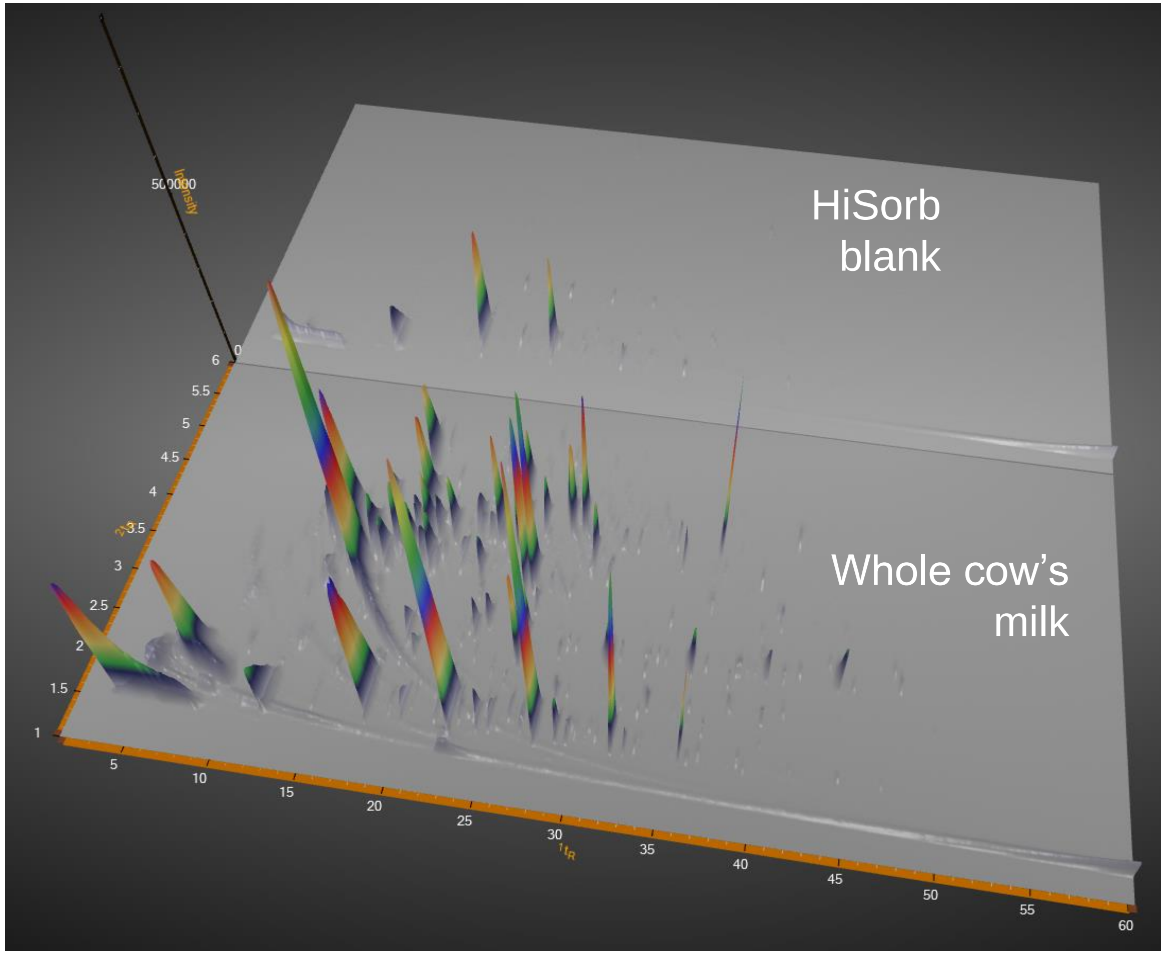
High-capacity sorptive extraction…with HiSorb

- Same principles as SPME but on a larger, more robust scale
  - ~100+ fold higher sensitivity
  - Robust & re-useable (>50 uses)

- Direct introduction of a sorptive material to the sample matrix simplifies and expedites the sampling process
  - Simple
  - Minimise sample prep stages
  - Selective
  - Immersive or headspace sampling

Flavour profiling of milk

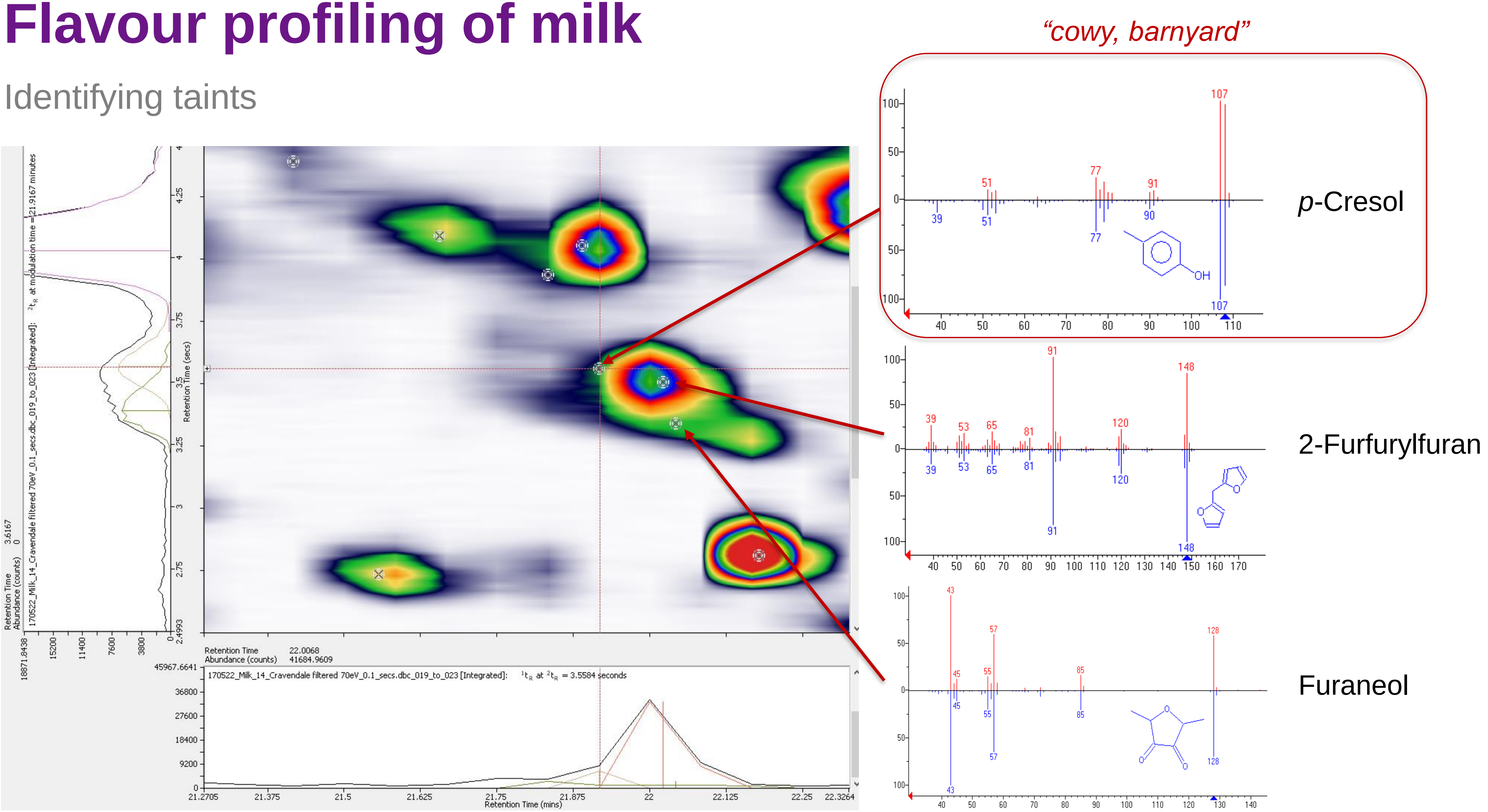
Centri – GCxGC - TOF



- Robust HiSorb probes for confident immersive sampling
- Enhanced separation by GC×GC
  - Siloxanes separated from compounds of interest

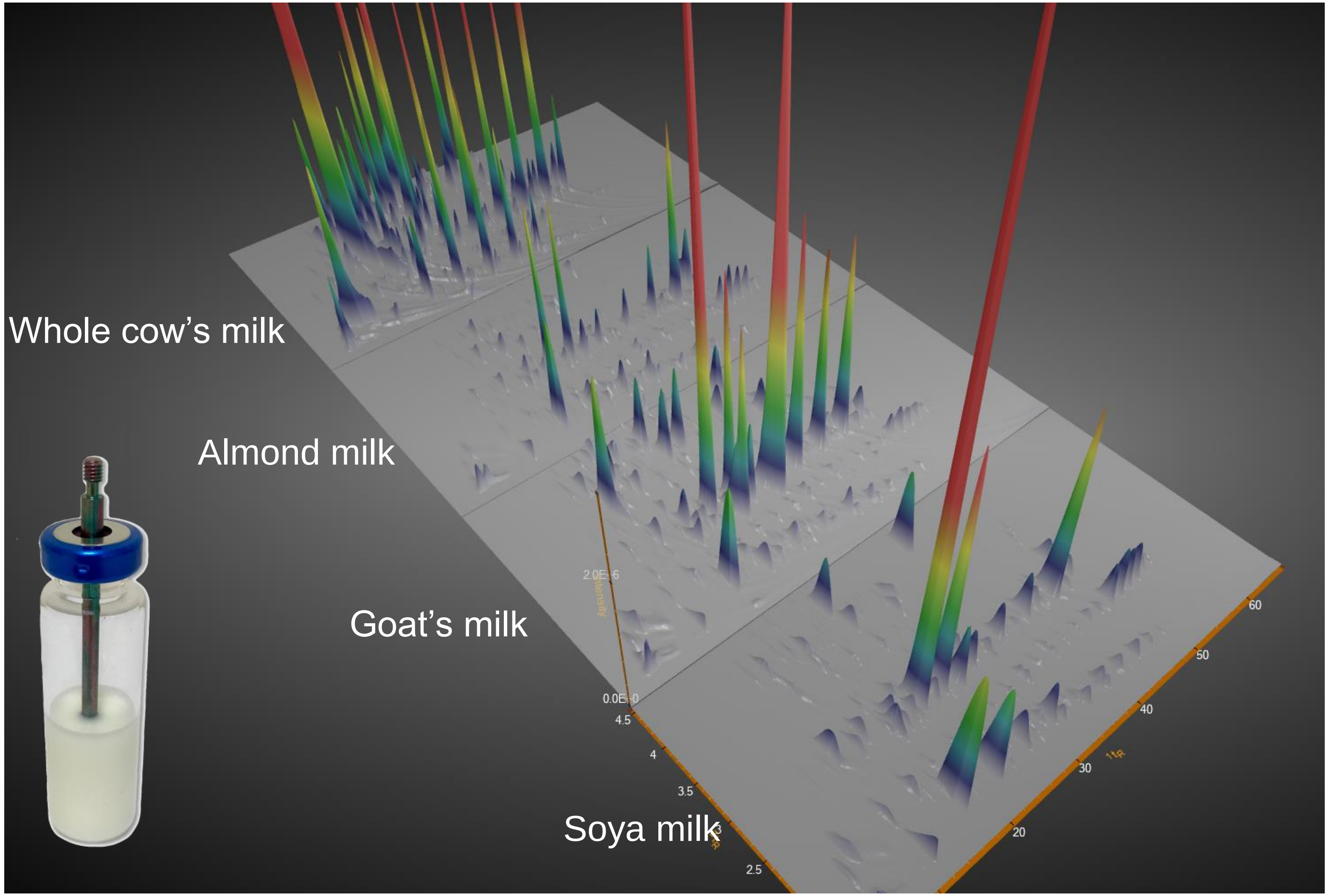
Flavour profiling of milk

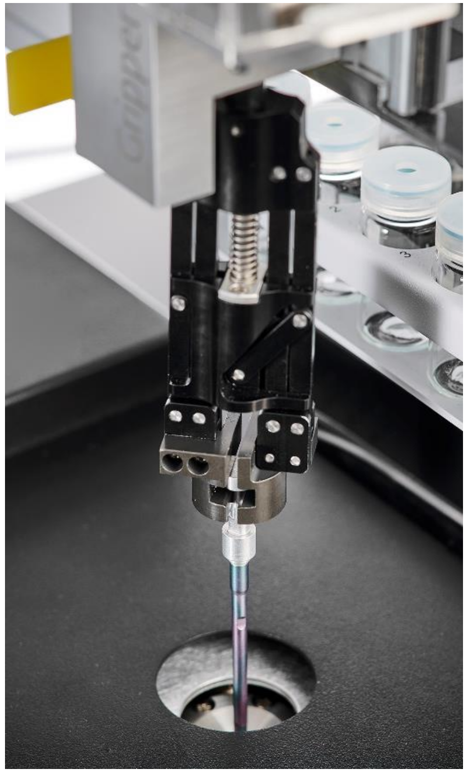
Identifying taints



Flavour profiling of milk

Automated sample preparation

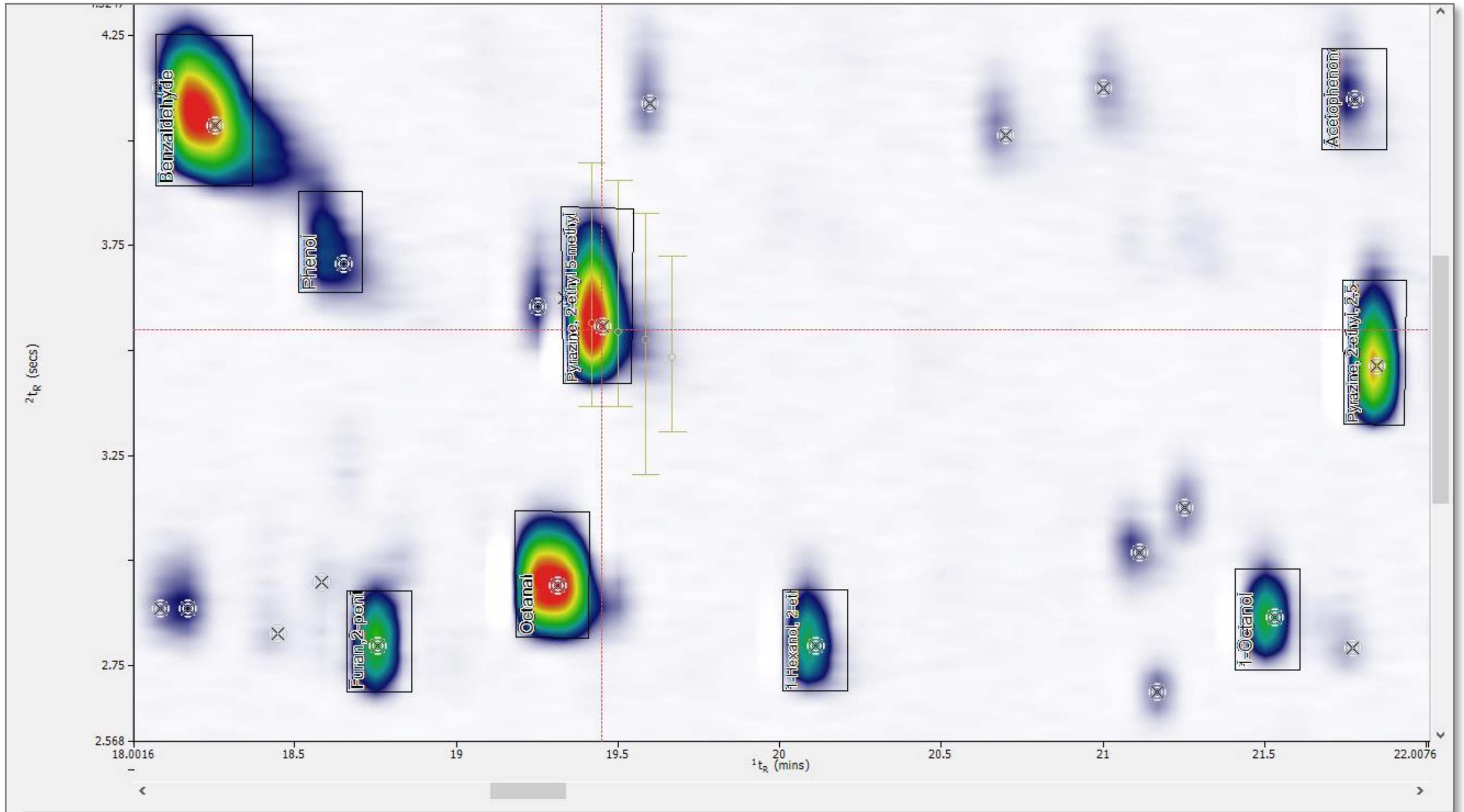




HiSorb probe in the automated wash station

Flavour profiling of milk

…using ChromSpace stencils



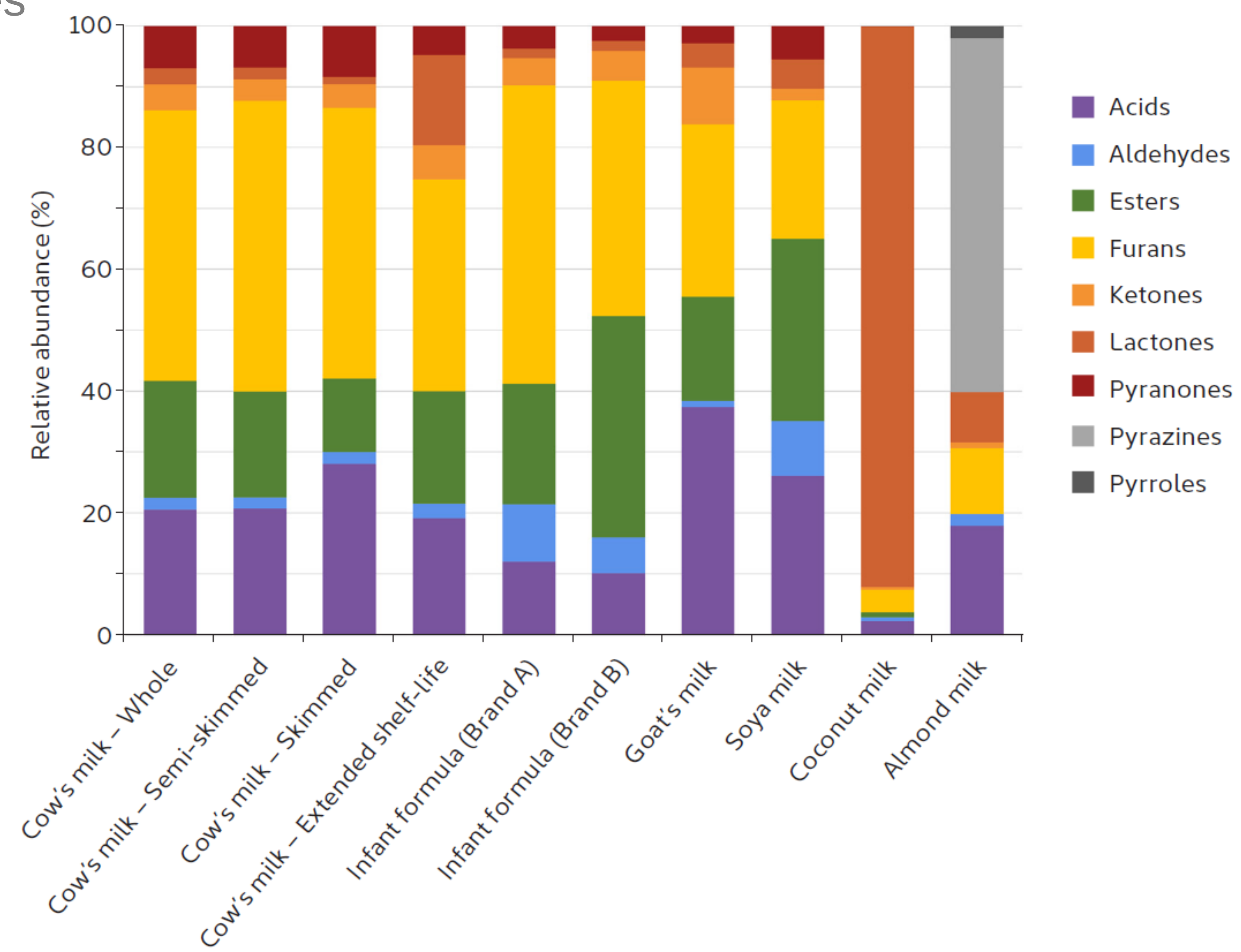
Area Percent | Num. Peaks 304

Source	Compound	MF	^1t_R	^2t_R	Area	Area %
DBC TIC	Undecanal	824	28.6667	2.8843	1.195E+05	0.12
DBC TIC	Furan, 2-pentyl-	819	18.7566	2.7956	2.30511E+05	0.24
DBC TIC	Benzaldehyde	810	18.2542	4.0346	1.3186E+06	1.37
DBC TIC	Hexanal	810	11.9861	3.0192	1.12298E+06	1.17

Flavour profiling of milk

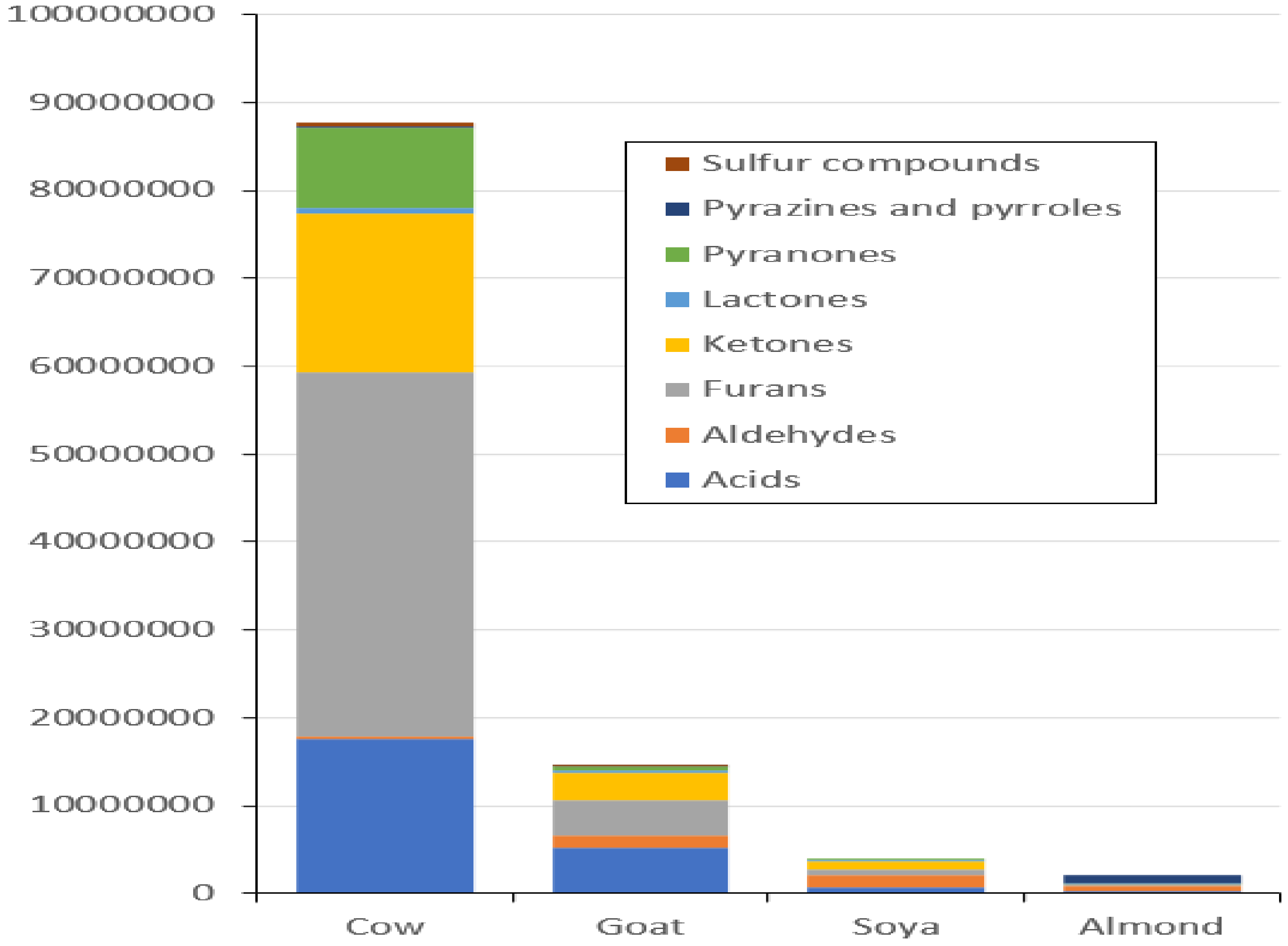
% composition of key chemical classes

- Coconut milk contains the highest composition of lactones and only sample to contain vanillin
- Almond milk was the only sample to contain numerous pyrazines



Flavour profiling of milk

Total peak area for target classes



- Soya and almond milk contained lowest VOC content when compared to cow's milk and goat's milk

Odorants in drinking water

Odorants in drinking water

Smelly water

- The most common complaint to water distribution companies relates to smelly water
- Odorants in water are monitored by SM 6040D method
- Some odorous compounds:
  - IPMP (Isopropyl methoxypyrazine)
    Asian ladybug smell
  - IBMP (3-Isobutyl-2-methoxypyrazine)
    Green bell-pepper smell
  - 2-MIB (2-Methylisoborneol)
    Unpleasant earthy, musty and mouldy aromas
  - 2,4,6 TCA (2,4,6-Trichloroanisole)
    Cork taint in wine can be smelt down to very low ppt levels
  - Geosmin (a hydroxylated decalin derivative)
    Its name is derived from the Greek for 'earth smell'

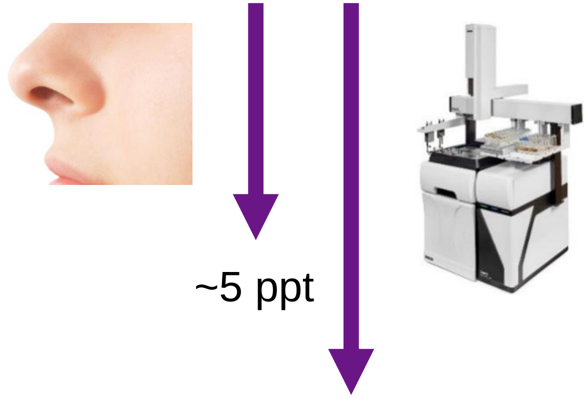
The human nose is able to detect compounds to very low levels

~5 ppt

Odorants in drinking water

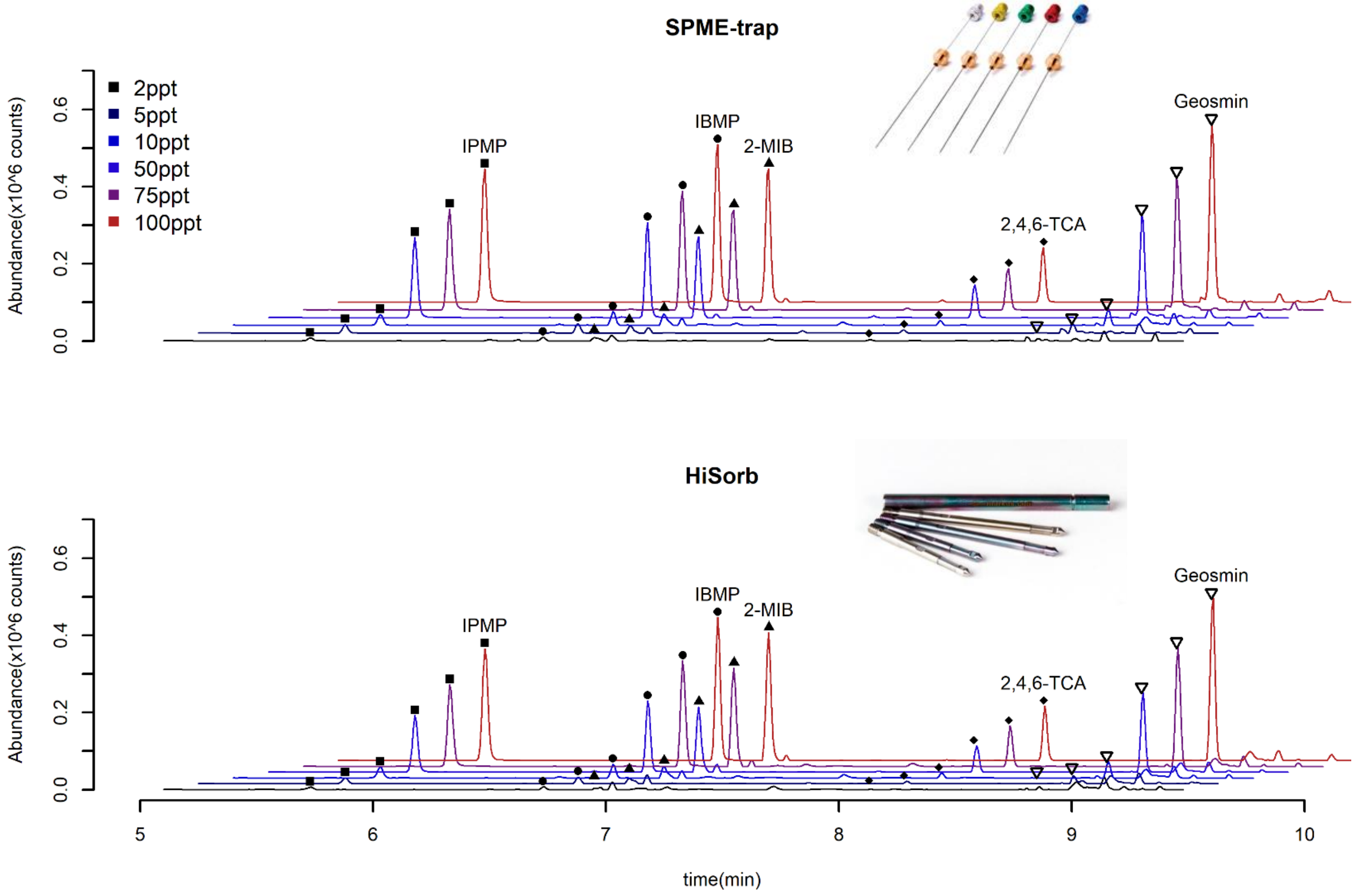
Comparing sorptive extraction methods

- Reaching lower limits with pre-concentration on stationary phase
- Comparison of SPME–trap with HiSorb
- Pre-concentration of odorants down to single-digit ppt



~5 ppt

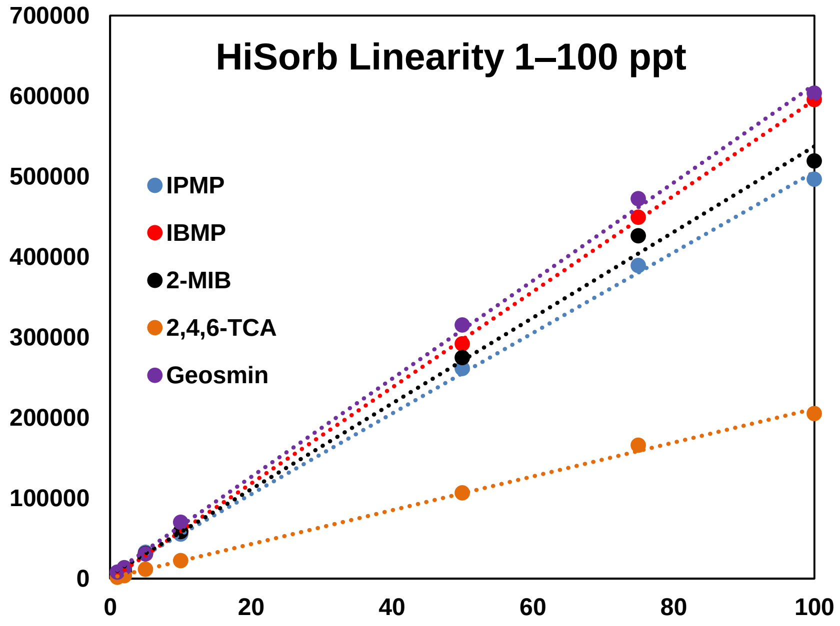
2 ppt



Odorants in water

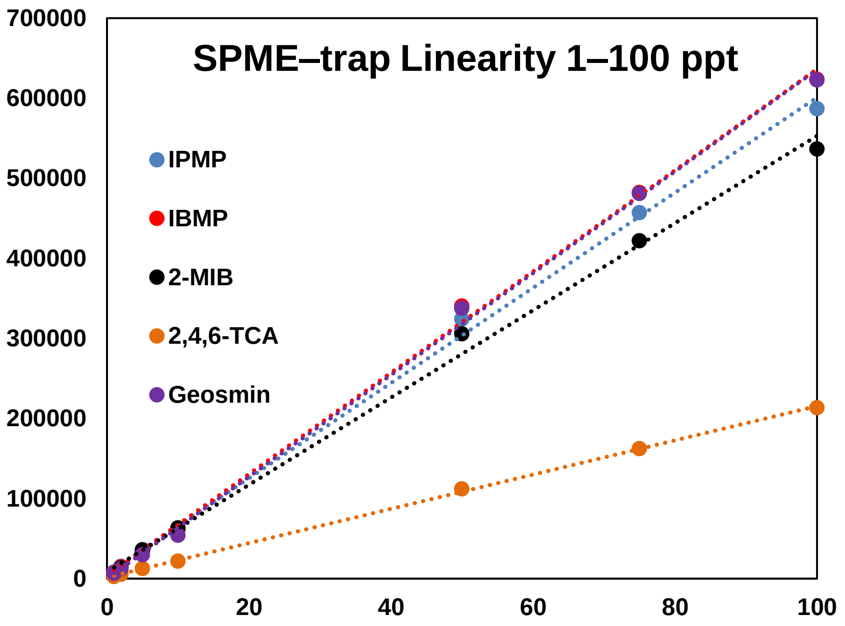
Reproducibility and linearity

- Centri showed excellent linearity R^2 and RSD for 9 consecutive runs
- Average recovery of 93% for SPME–trap and 110% for HiSorb
- Centri meets the performance required by SM 6040D



R^2 0.9990

RSD <8%



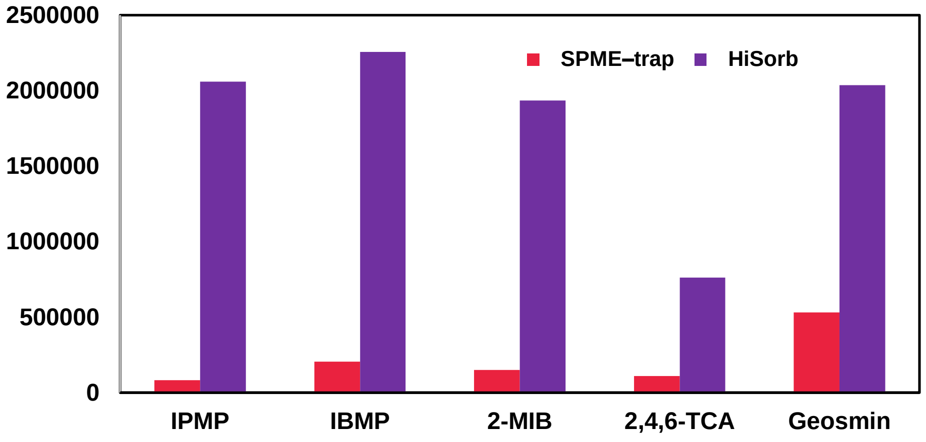
R^2 0.9981

RSD <5%

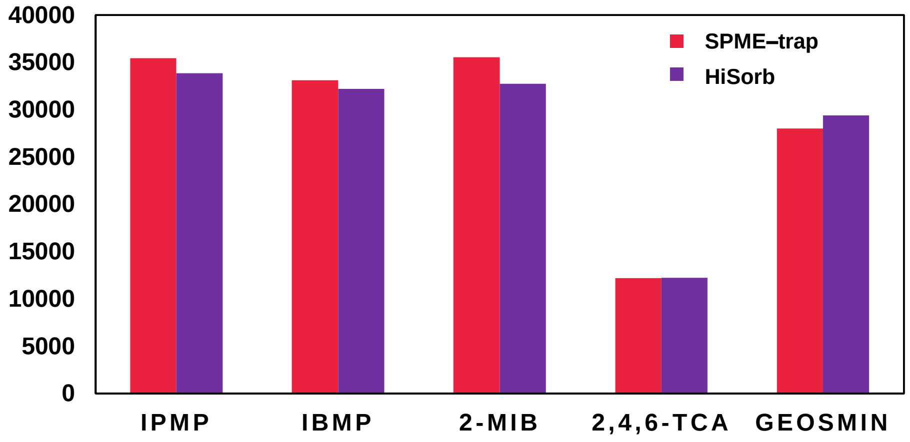
SPME-trap fibers: DVB/CAR/PDMS
HiSorb: Only PDMS

Odorants in drinking water

SPME–trap vs. HiSorb



SPME–trap fibers: Only PDMS
HiSorb: Only PDMS



SPME–trap fibers: DVB/CAR/PDMS
HiSorb: Only PDMS

Increased sensitivity

- Detection limits are lower than for SPME–trap because of the larger capacity of the PDMS sorbent.
- HiSorb can be used for immersive or headspace sampling of liquids and solid samples

Time and cost savings

- Robust, easy-to-use probes allow unattended sample preparation and maximum productivity.
- HiSorb is easier and quicker to use than solvent extraction.
- Re-usable probes and tubes minimise the cost per sample.
- The cost of solvent consumption and disposal is eliminated.

Odorants in drinking water

Prep-ahead functionality

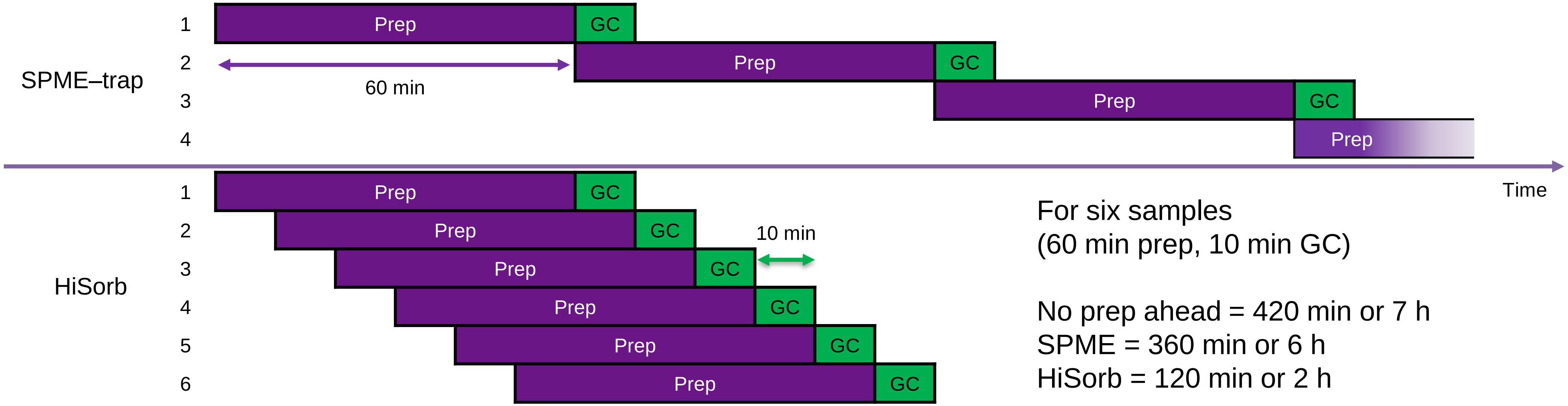
Probe storage keeps probes clean and ensures conditioned probes are ready to be used.

The robot inserts the probe into the vial and the assembly is incubated/agitated to ensure analyte equilibration.

The probe is removed from the vial and a wash/dry station removes the residual sample matrix.

The probe is thermally desorbed and the vapours transferred to the focusing trap.

The trap is thermally desorbed at up to 100˚C/s in inject the sample into the GC-MS system.



For six samples
(60 min prep, 10 min GC)

No prep ahead = 420 min or 7 h
SPME = 360 min or 6 h
HiSorb = 120 min or 2 h

Semi-volatile compounds in air and in water

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PAHs in the environment

SVOCs with Centri

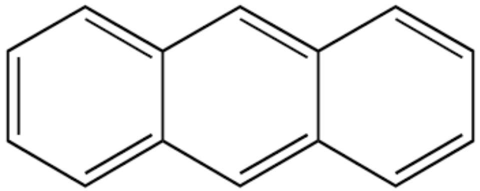
- PAHs are carcinogenic, mutagenic and teratogenic properties
- They need to be monitored both in air and in water
- Traditionally:
  - Solvent extracted
  - Preconcentrated via rotary evaporation

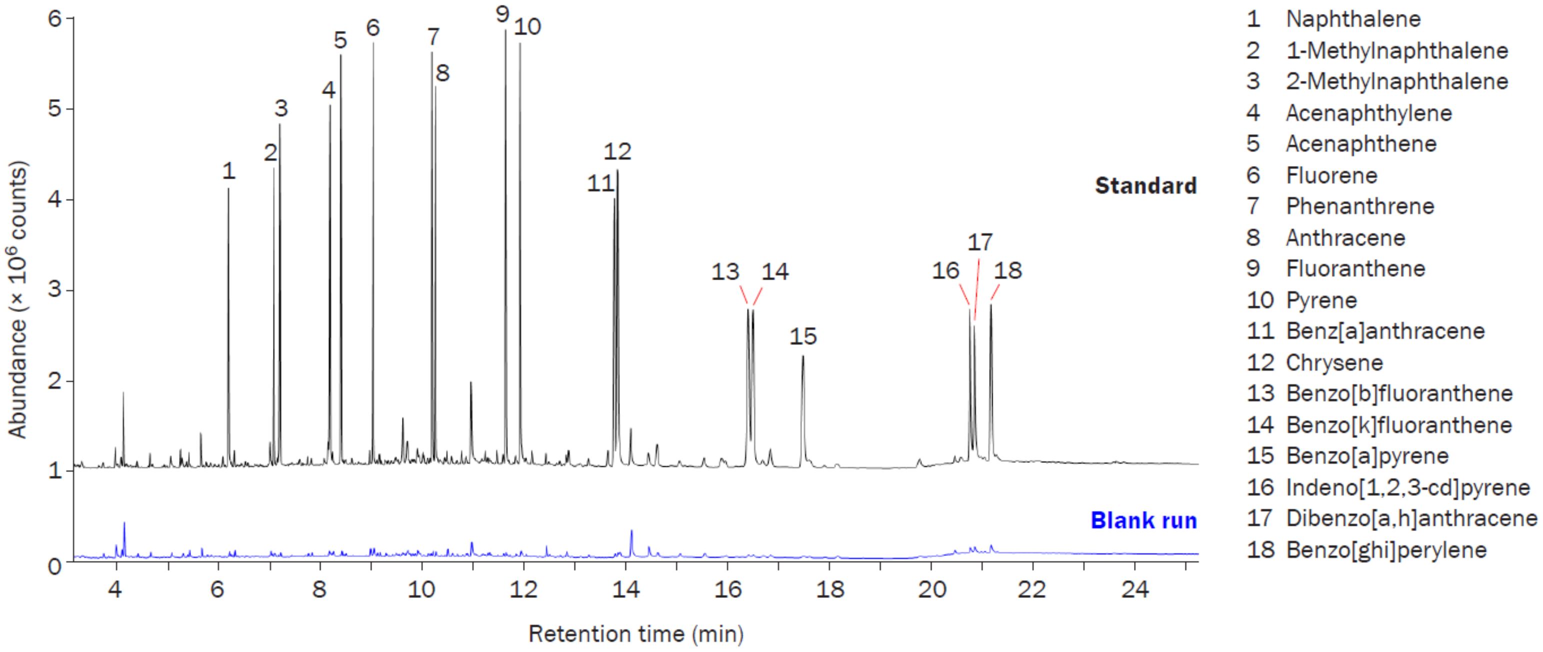
- Centri offers
  - TD-50 module
  - HiSorb immersive
    for versatile PAHs analysis

PAHs in air

SVOCs with Centri

- Sample-path temperature uniformity allows analysis of VOCs and SVOCs on the same platform, without modifications.

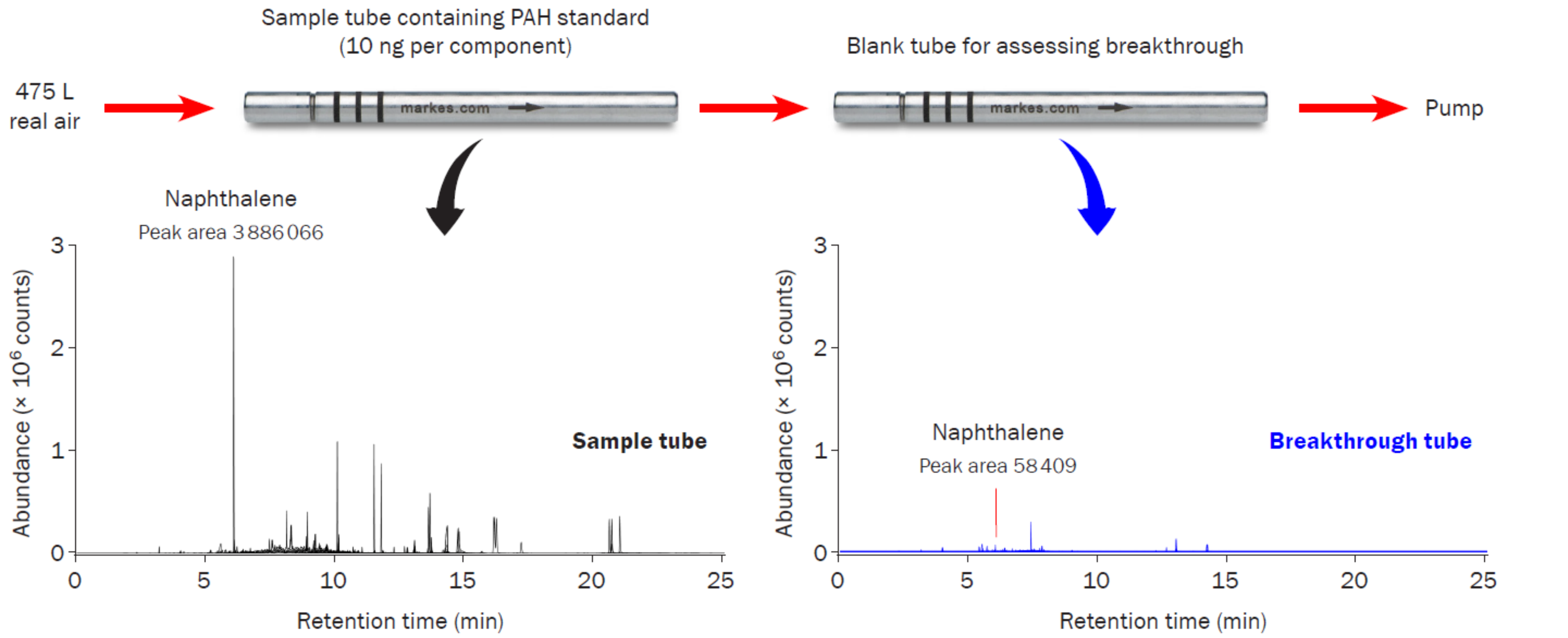




Application note 139

PAHs in air

Breakthrough analysis

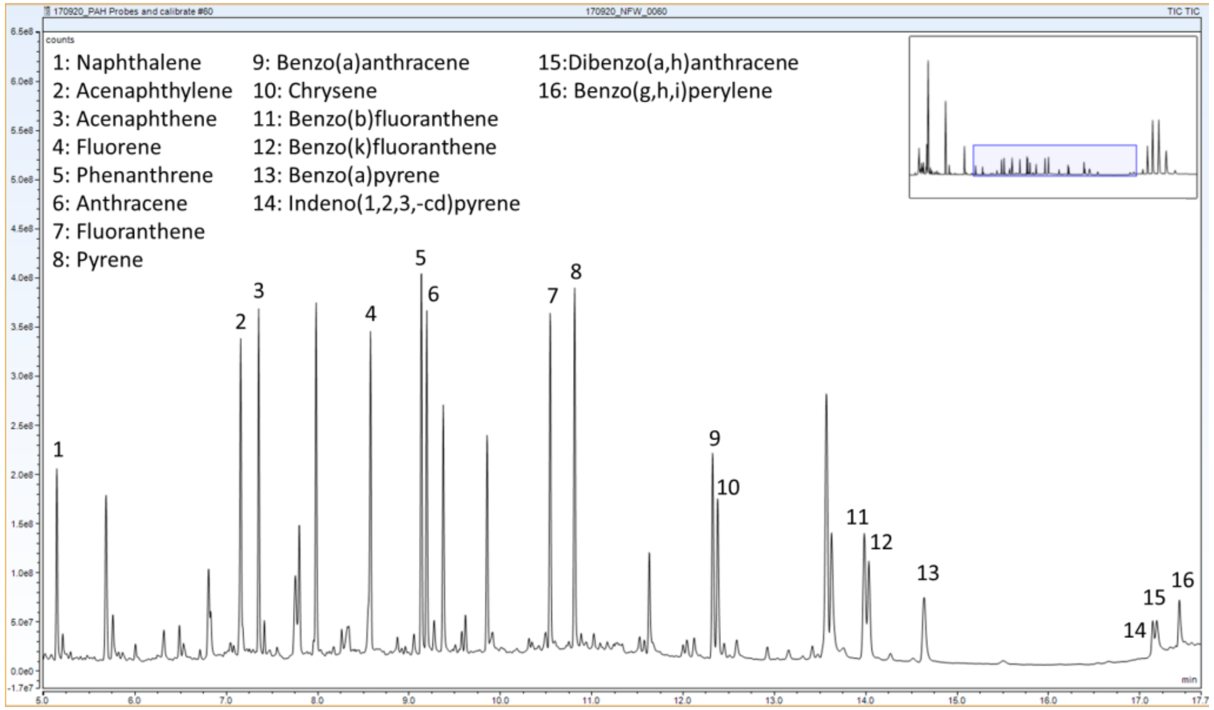


Only 1.5% of Naphthalene broke through

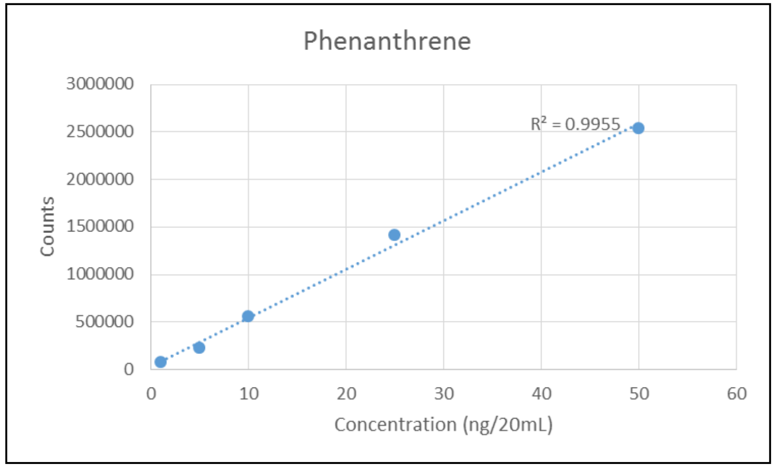
PAHs in water

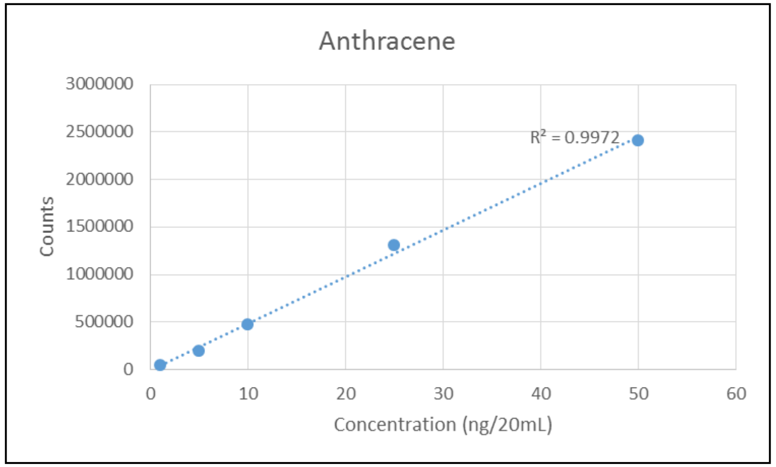
SVOCs with Centri

- US EPA Method 610 requires the monitoring of PAHs
- Boiling points: 218–500°C
- 2.5 ppb in water
- Immersive extraction
- PDMS sorptive phase



Examples of extraction linearity





Low-level odorants in wine by automated HiSorb

Odorants in wine

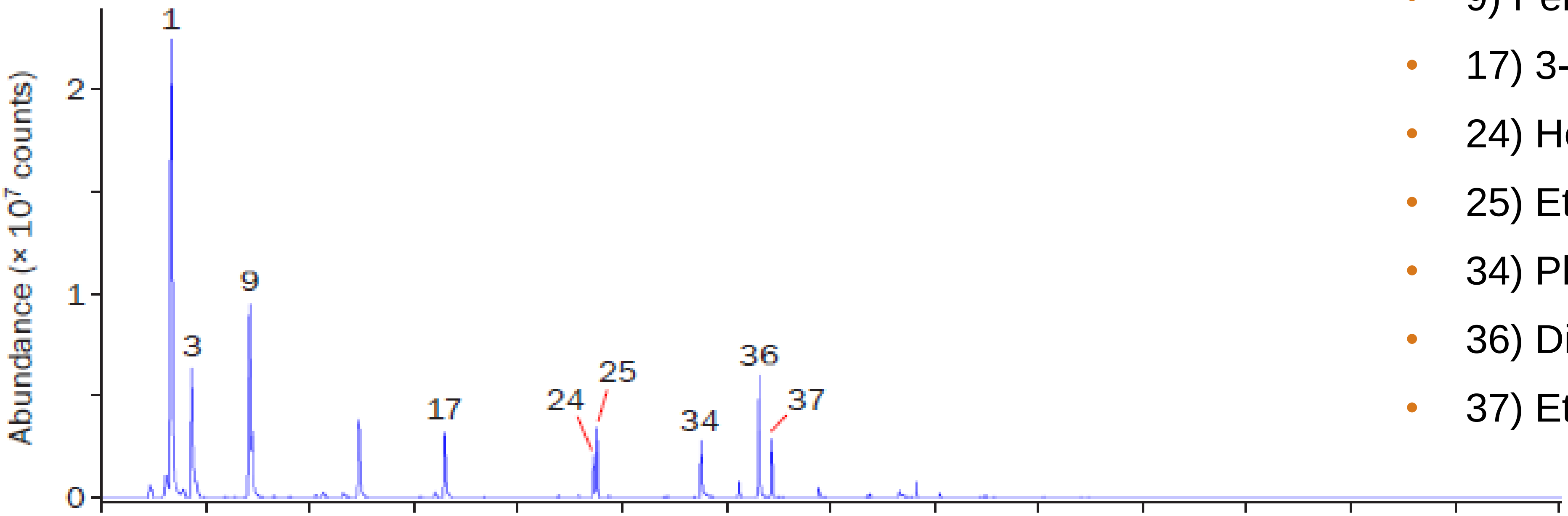
Produced by yeast

- The yeast *Brettanomyces* (*Dekkera*) *bruxellensis* (‘Brett’)
- Its growth results in the production of:
  - 4-ethylphenol (4-EP)
  - 4-ethylguaiacol (4-EG)
- These have unpleasant odours:
  - ‘medicinal’, ‘phenolic’ or ‘horse sweat’
  - masking fruity aromas
- Goal is to identify a range of VOCs in red wine, including 4-EP and 4-EG

Odorants in wine

HiSorb analysis of wine

- High split: 50 mL/min
- TargetView for deconvolution and background subtraction



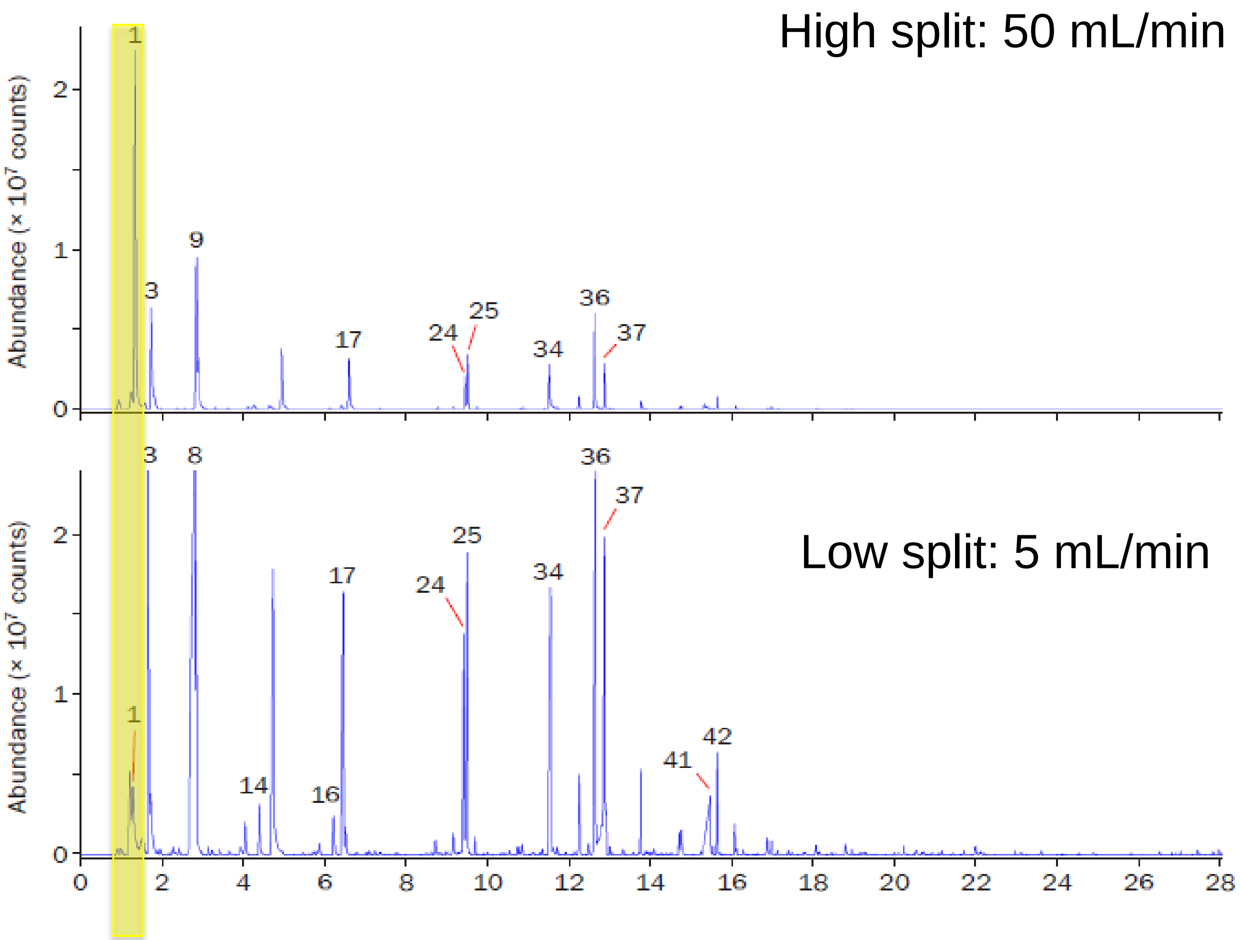
- 1) Ethanol
- 3) Ethyl acetate
- 9) Pentan-1-ol
- 17) 3-Methylbutyl acetate
- 24) Hexanoic acid
- 25) Ethyl n-hexanoate
- 34) Phenylethyl alcohol
- 36) Diethyl butanedioate
- 37) Ethyl n-octanoate

Odorants in wine

HiLow analysis

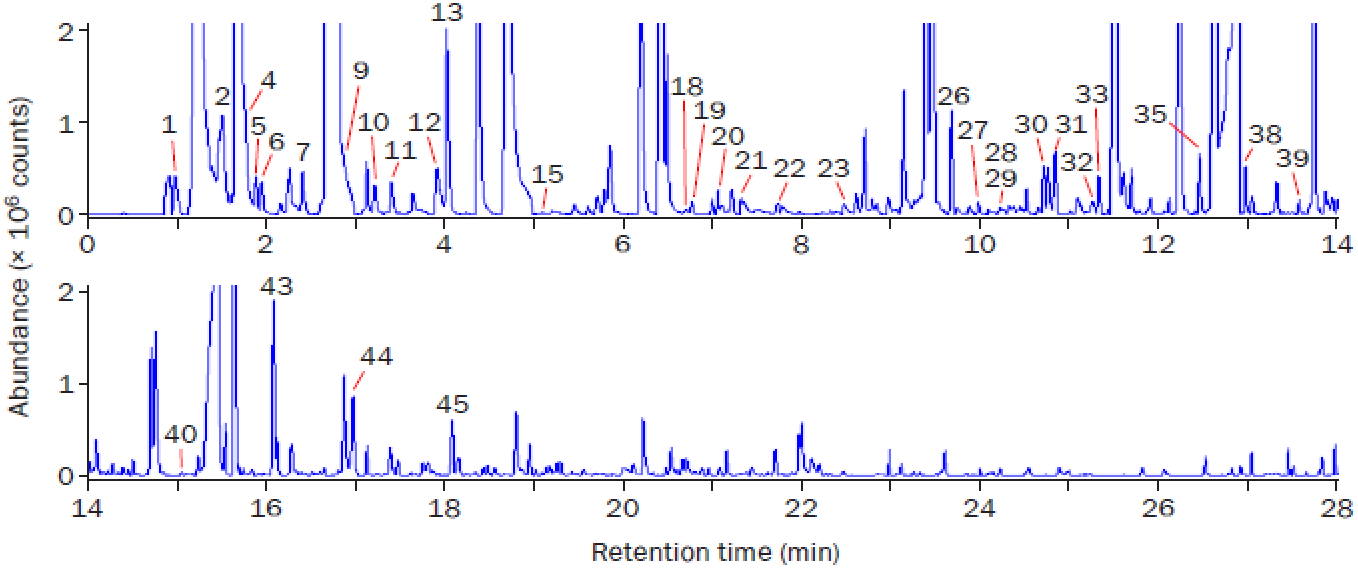
Reduction of Ethanol

- hydrophobic sorbents in the focusing trap
- Purging the focusing trap
- Use of a low split ratio



Odorants in wine

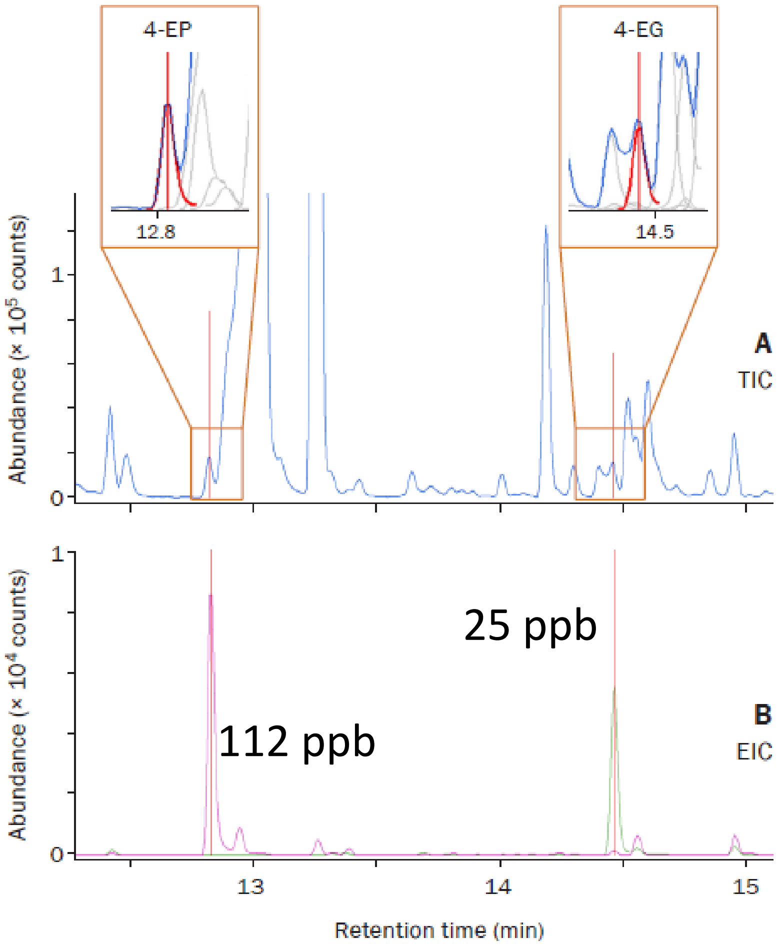
Expanded HiLow analysis



1 Ethanol
2 3-Methylfuran
3 Ethyl acetate
4 2-Methylpropan-1-ol
5 3-Methylbutanal
6 Benzene
7 n-Propyl acetate
8 1,1-Diethoxyethane
9 Pentan-1-ol
10 Toluene
11 2-Methylpropyl acetate
12 Hexanal
13 Ethyl butanoate
14 Ethyl 2-hydroxypropanoate
15 Furfural
16 Hexan-1-ol
17 3-Methylbutyl acetate
18 Styrene
19 Non-1-ene
20 Heptanal
21 γ-Butyrolactone
22 3-Methylbutan-1-ol
23 Benzaldehyde
24 Hexanoic acid
25 Ethyl n-hexanoate
26 n-Hexyl acetate
27 2-Ethylhexan-1-ol
28 1-Phenylpropyne
29 Benzeneacetaldehyde
30 Acetophenone
31 Octan-1-ol
32 Linalool
33 Nonanal
34 Phenylethyl alcohol
35 2-Ethylphenol
36 Diethyl butanedioate
37 Ethyl n-octanoate
38 Decanal
39 Ethyl phenylacetate
40 Ethyl phenylpropanoate
41 n-Decanoic acid
42 Ethyl n-decanoate
43 Ethyl 3-methylbutyl butanedioate
44 n-Dodecane
45 Ethyl n-dodecanoate

Odorants in wine

Malodours in wine

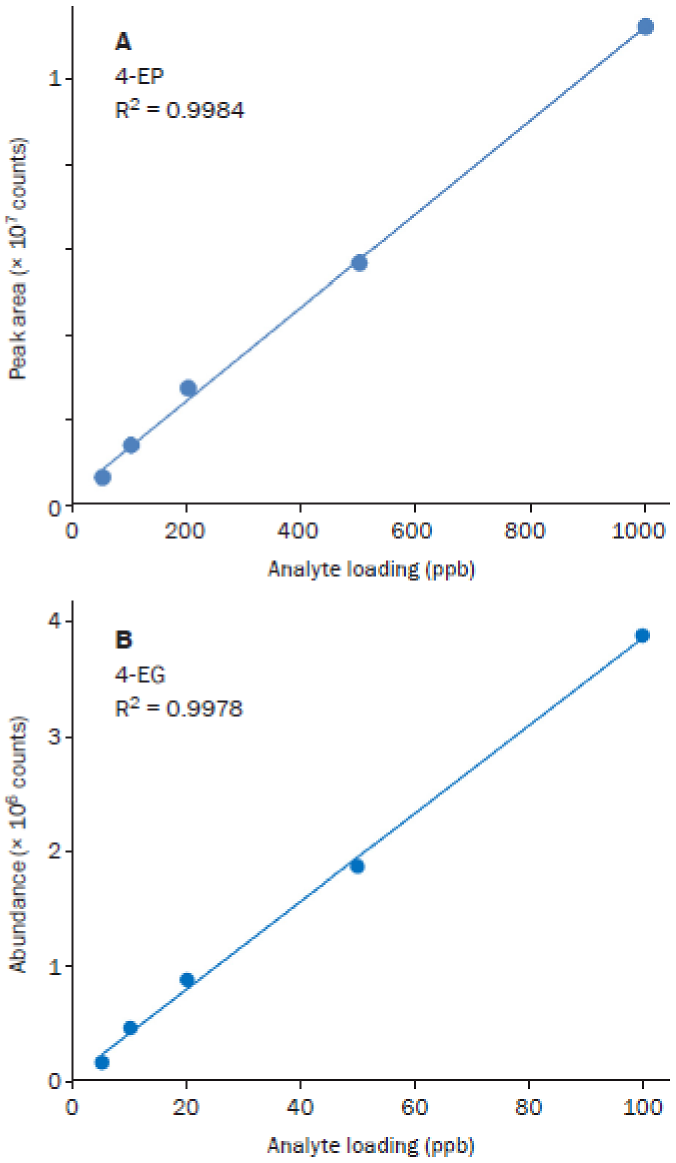


4-EP

300–600 ppb low-ppb levels

4-EG

50 ppb sub-ppb



MARKES international

Identifying odour taints in pet food

IngenieríaAnalítica Chromatography & Spectrometry

A company of the SCHAUENBURG International Group

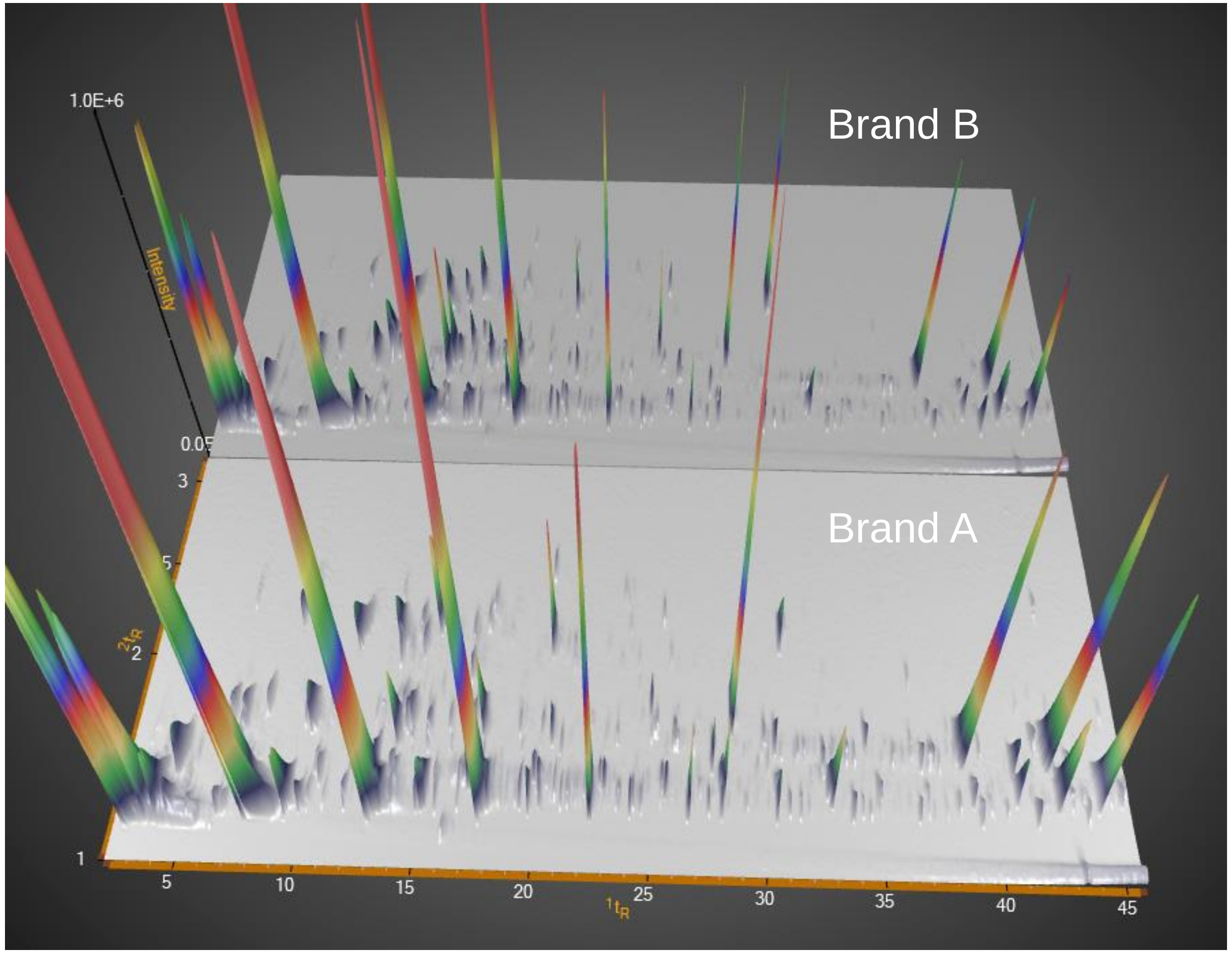
Odour taints in pet food

Background

- Palatability
  - Why ‘brand A’ over ‘brand B’?

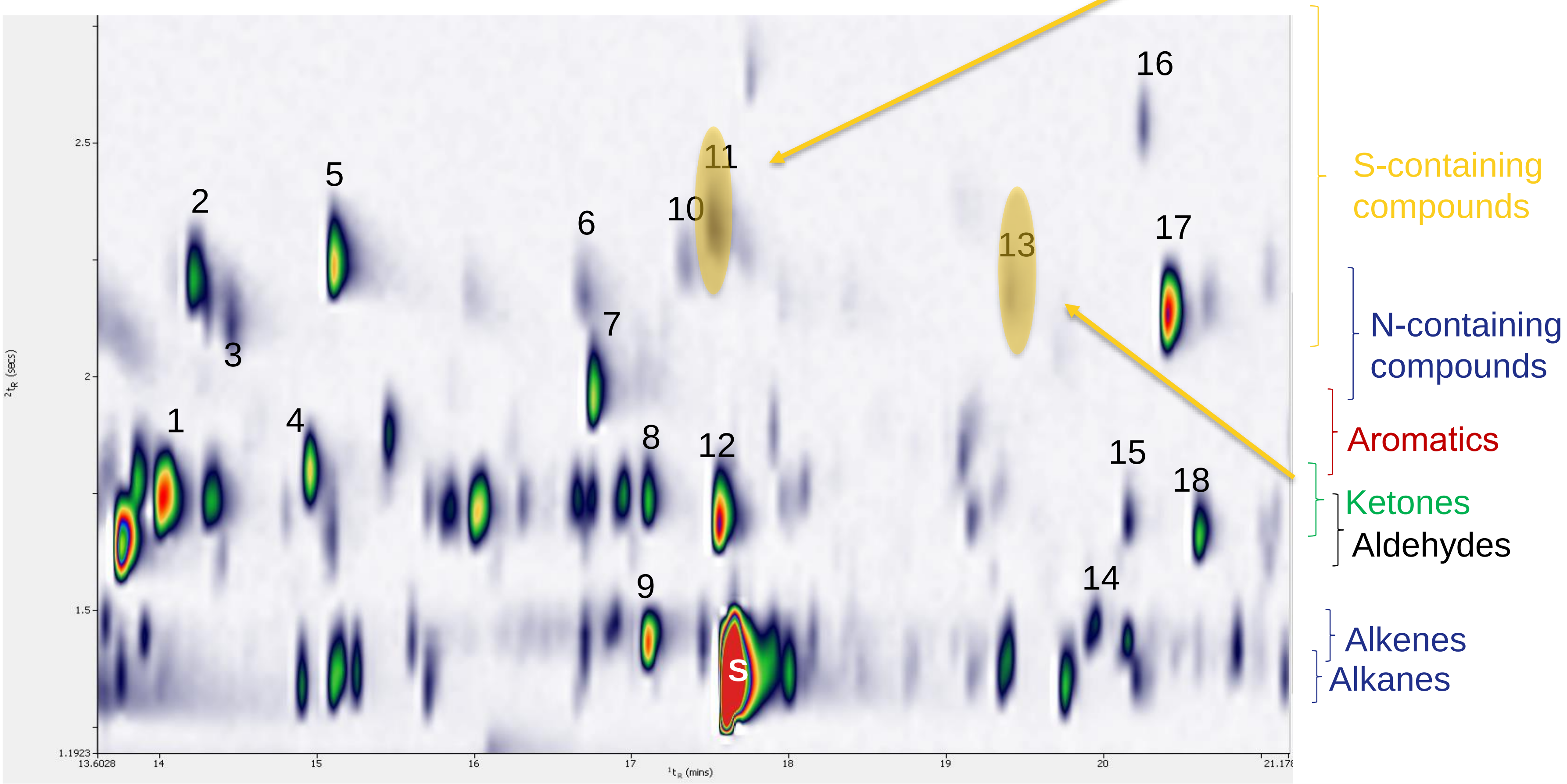
Odour taints in pet food

Analysis by Centri-GC×GC-TOF MS



Odour taints in pet food

Enhanced separation of trace sulfurs

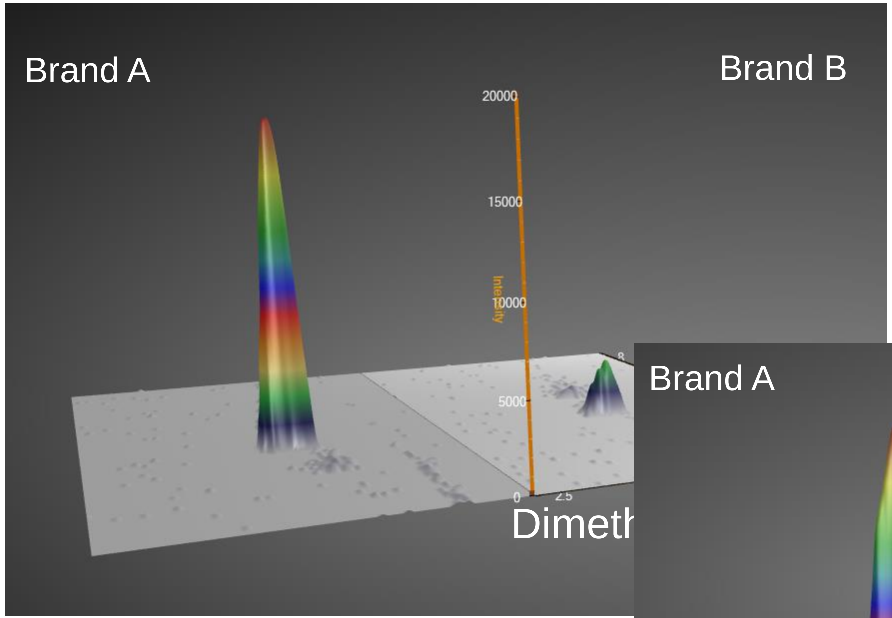


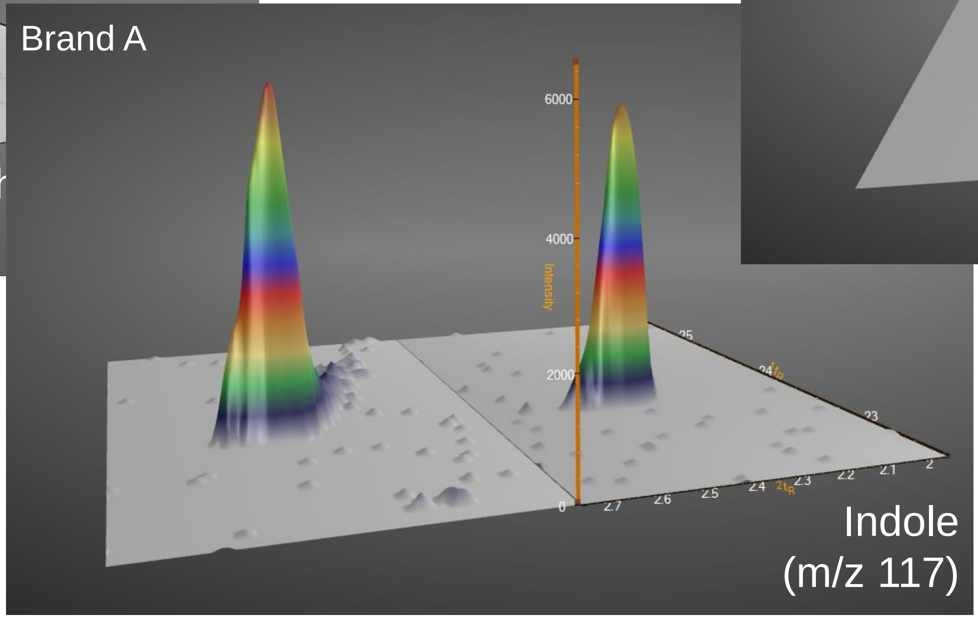
1 Octanal
2 2-Methyltetrahydrothiophen-3-one
3 2-Ethyl-3-methyl pyrazine
4 Benzene, 1,2,4-trimethyl-
5 2-Acetyl thiazole
6 Acetophenone
7. 2,5-Dimethyl 3-ethyl pyrazine
8. 2-Nonanone
9. Undecane
10. 5-Methyl-2-formylthiophene
11. 2-Acetyl thiophene
12. Nonanal
13. 2-Acetyl-3-methyl thiophene
14. 1-Dodecene
15. 2-Decanone
16. 1,2-dithian-4-one
17. Kahweofuran
18. Decanal

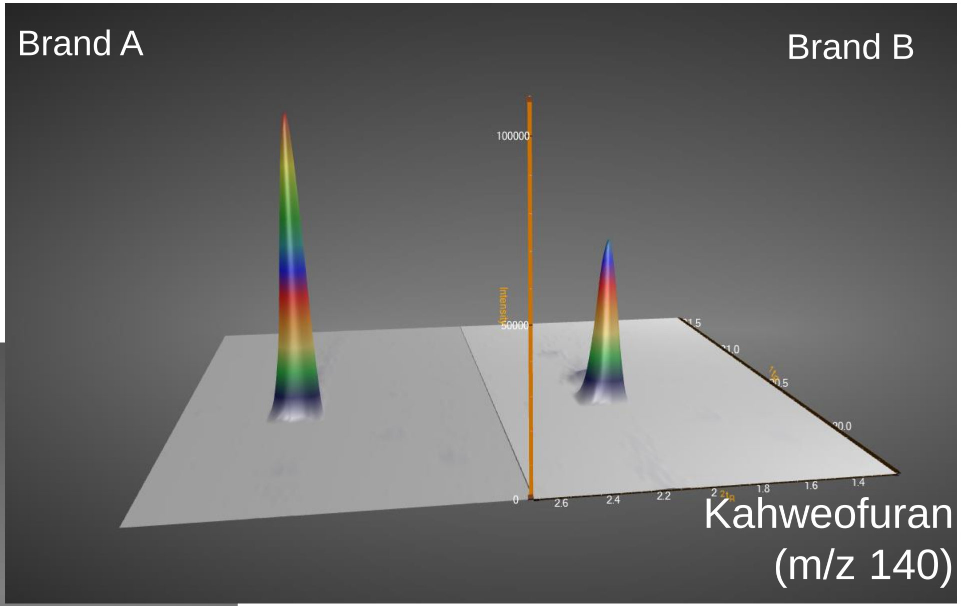
- These odorous compounds would have co-eluted with higher-loading species in 1D GC-MS

Odour taints in pet food

Comparison of aroma volatiles

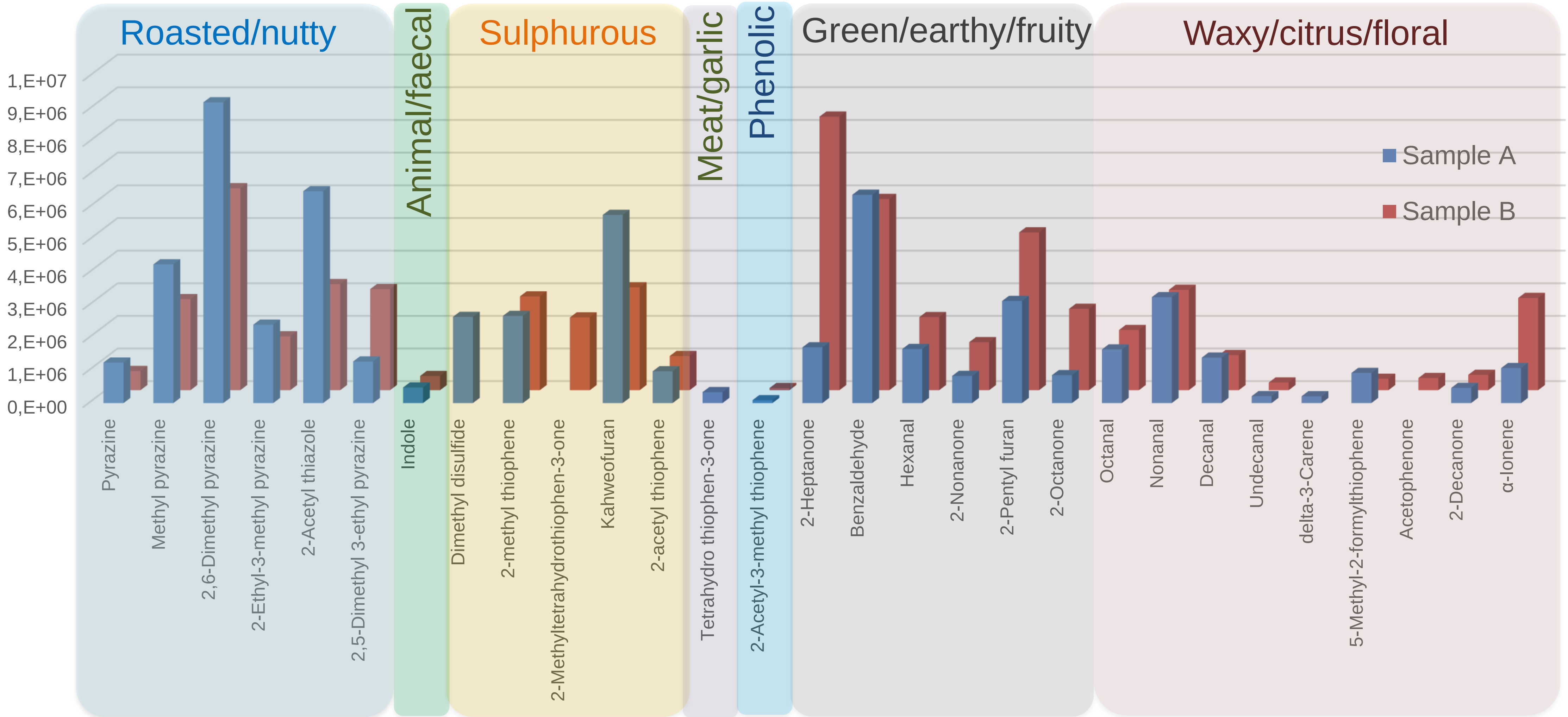






Odour taints in pet food

Comparison of aroma volatiles



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Questions?

What can we offer

Approaches to handling the analysis of water

Challenges include:	Solutions we can offer with Centri:	Benefits
High sample number	• Full automation • Re-collection	Saves time / money
High contaminant levels (e.g. waste water)	• Classic headspace • Multi-bed sorbent • Large split range (1:125,000)	One instrument for all
Low contaminant levels (e.g. drinking water)	• Multi-bed sorbents • SPME fibre preconcentration • Trapping capabilities • Multiple injection modes • Multiple enrichment steps • Splitless analysis	Confidence in the results
Different sample types: • Drinking water • Waste water • Slurry water	• SPME / HiSorb / Classic headspace / Matrix modification • Classic headspace / HiSorb • HiSorb	One instrument for all
Wide analytical target list from VVOCs to SVOCs	• Multi-bed trap • SPME fibre preconcentration • Multiple injection modes	Saves time
Reproducibility	• Trapping capabilities • Re-collection	Confidence in the results
Sample traceability	• TubeTAG (RIFD) • Barcode scanner	Confidence in the results

Centri