MARKES international

THE QUEEN'S AWARDS FOR ENTERPRISE: INTERNATIONAL TRADE 2015

Completely Cryogen-free monitoring of
- PAMS Ozone Precursors,
- TO-15 Air Toxics and
- OVOCs
in Ambient Air in a Single Run

Jan Peter Mayser, Ph.D.; Nicola Watson, Ph.D.

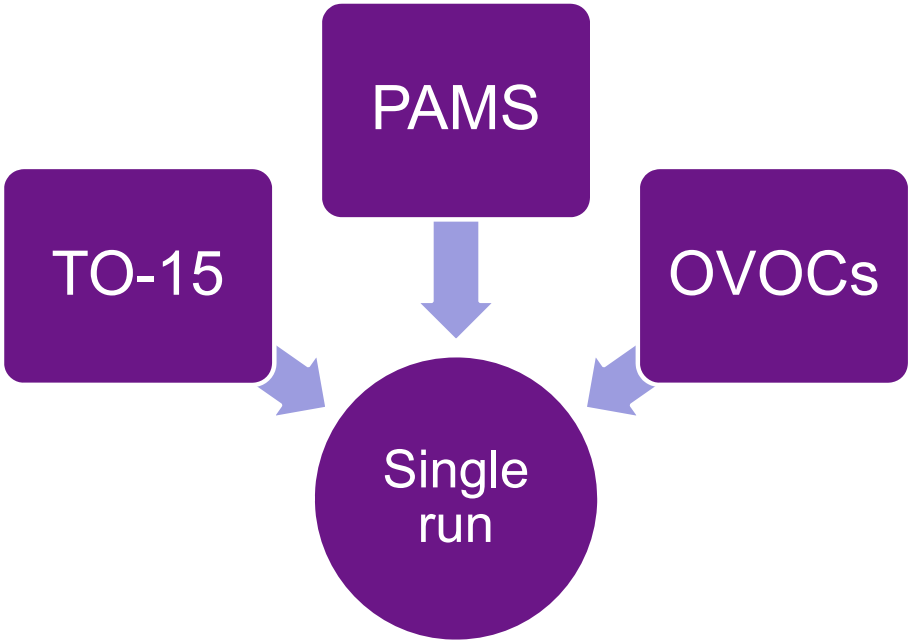
PAMS + TO-15 + OVOCs

Outline

- Why monitor VOCs?
- Challenges

- Solution
  - Pre-concentration
  - Water management
  - GC with FID & MS detection

- Results
- Summary



Why monitor VOCs in Air

Environmental and public health ⇒ regulations ⇒ standard methods

- Key organisations:

US EPA Method TO-15 (canister)
US EPA Method TO-17 (pumped tube)
US EPA Method 325 (passive tube)
US EPA Guidance on ozone precursor monitoring (on-line)

ISO 16017-1 (pumped tube)
ISO 16017-2 (passive tube)

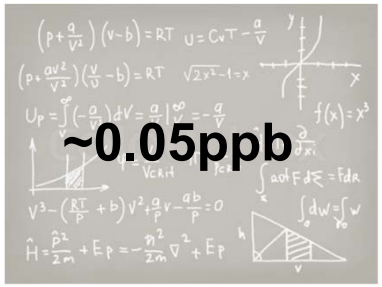
ASTM D6196 (pumped and passive tube)
ASTM D5466 (canister)

13th five year plan: Reduce VOC emissions

- Urban Air Monitoring
- Industrial Air monitoring
- VOC reduction

The first challenge of VOC monitoring in air

VOCs are harmful to human health at very low levels



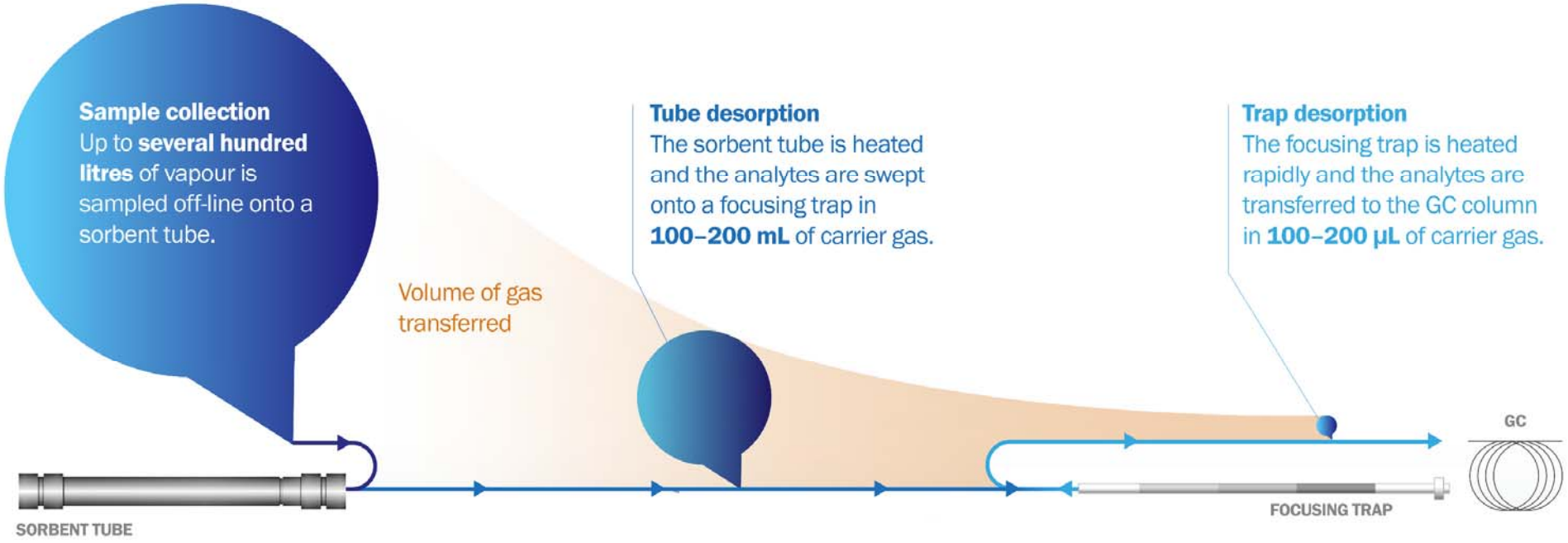
WHO benzene guidelines – Air

- Benzene is carcinogenic to humans and no safe exposure limit can be recommended
- General guidance: Concentrations of airborne benzene associated with an excess lifetime risk of leukaemia of…
  - 10^{-4} = 17µg/m^3
  - 10^{-5} = 1.7µg/m^3
  - 10^{-6} = 0.17µg/m^3

The solution to reach these low levels?

Pre-concentration using Thermal Desorption

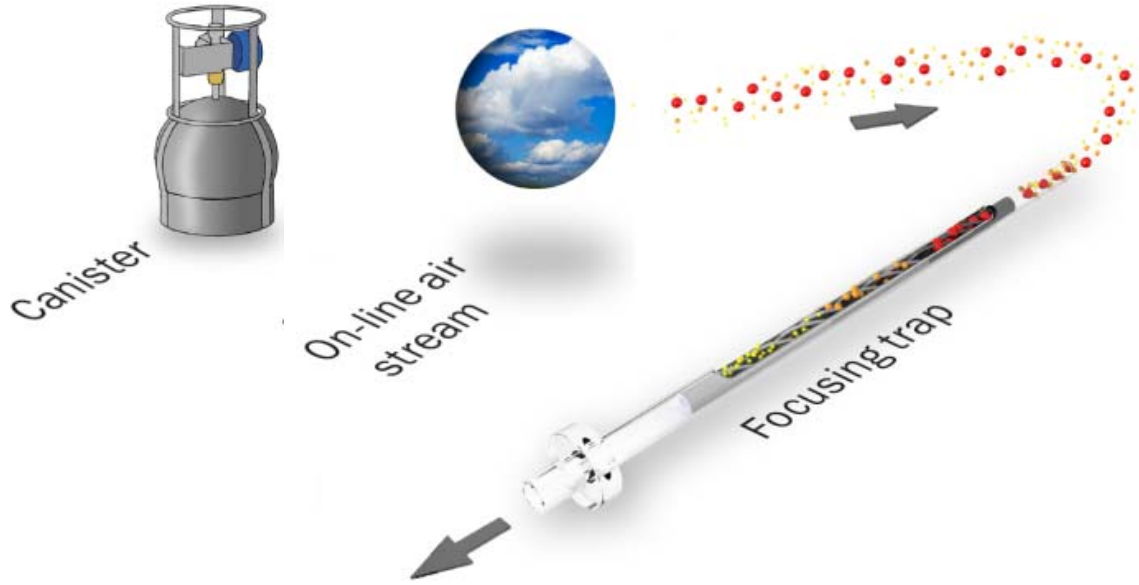
Thermal desorption



Stage 1: Sample concentration

Whole air analysis of VVOCs, VOCs and OVOCs

- Whole air, or canister, samples are introduced directly to the focusing trap at controlled flows.
  - Focusing trap sorbents and temperatures can be set to allow water and other interferences to pass through unretained.
  - For true water removal sample streams can be passed through cryogen-free water removal devices before analyte focussing.

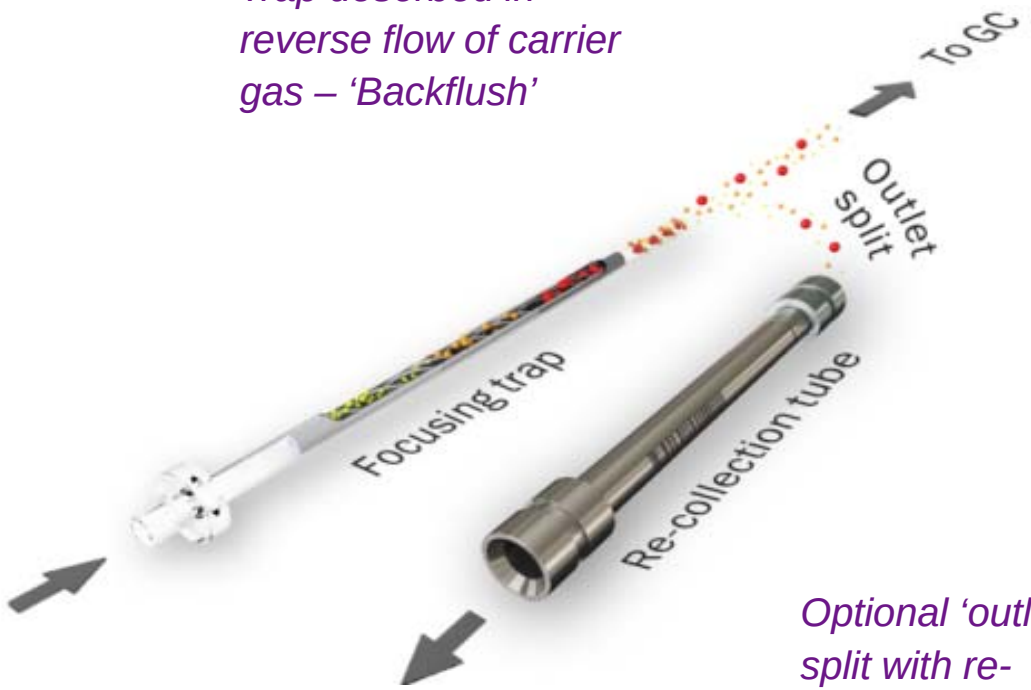


Stage 2: Trap desorption and GC(MS) injection

Whole air analysis of VVOCs, VOCs and OVOCs

- Once the VVOC & VOC present in the sample have been focussed, the trap is rapidly heated, at rates up to 100°C s^{-1}, in a reverse flow of carrier gas.
- Retained compounds are released and injected into the GC in a narrow band of vapour.
- Excellent chromatography and low detection limits are achieved.

Trap desorbed in reverse flow of carrier gas – 'Backflush'

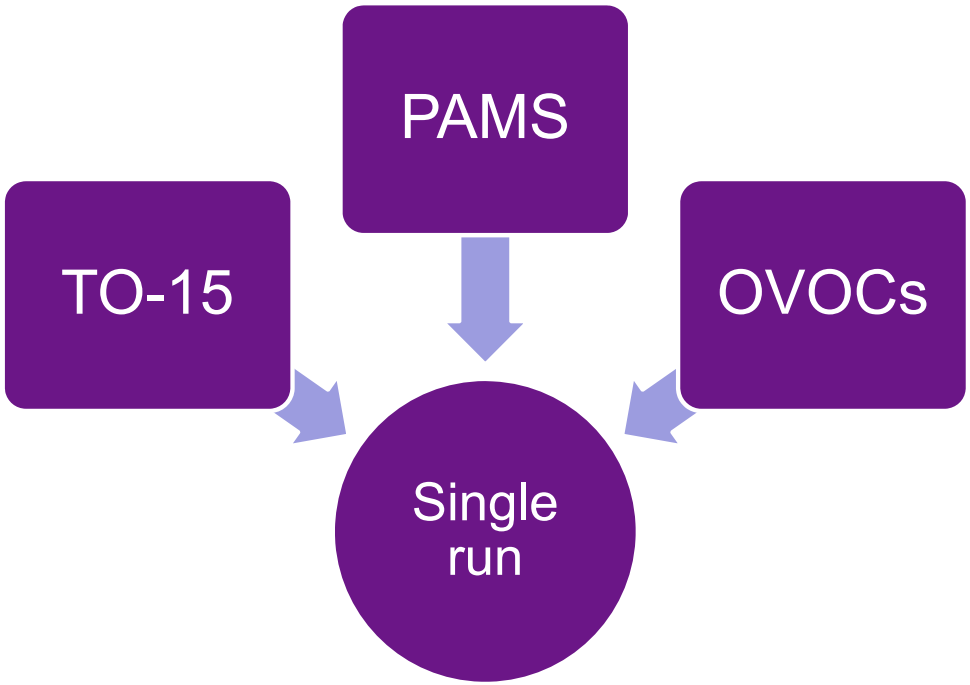


Optional 'outlet' split with re-collection

The newest challenge in air monitoring

Obtaining double the data in the same amount of time

- Combining 3 target lists
- Total of 117 compounds in 1 hour
- Mandatory in China but of growing interest worldwide
- Integrating the analysis of formaldehyde by TD-GC-MS, without derivatisation

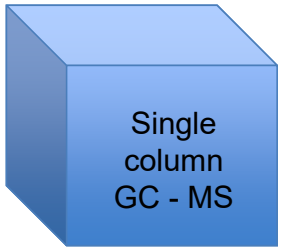


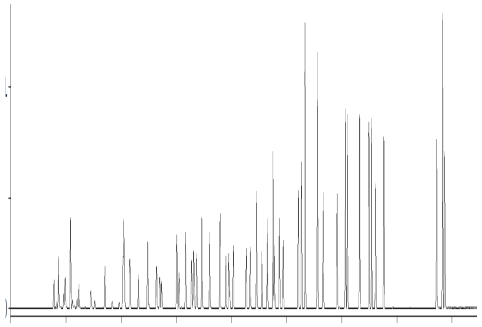
TO-15

Air toxics

- Comprise of polar and non-polar VOCs, as well as a range of halogenated compounds
- The atmosphere is sampled by introduction of air into a specially-prepared stainless steel canister
- Pre-concentration is key

TO-15
from C_3





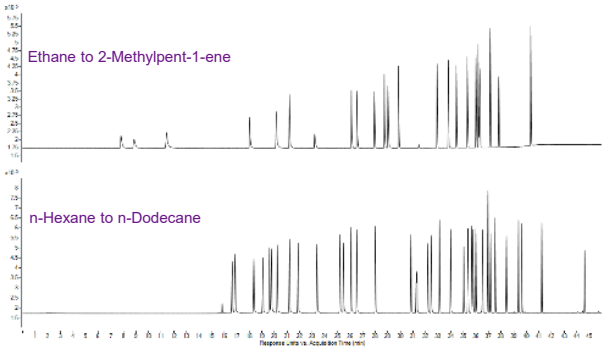
PAMS

Photochemical Assessment Monitoring Scheme (PAMS)

- VOCs and NOx play a pivotal role in the creation of ground-level ozone.
- Usually polar species are not of interest although this is changing, especially in USA.
- Water management is key, especially if polar, alcohols & pinenes are of interest as Nafion dryer can't be used.

Ozone Precursors C_2-C_{12}

Dual column GC - FID



OVOCs

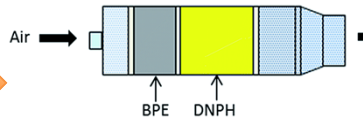
Oxygenated volatile organic compounds

- Resource-hungry workflow; usually analysed via TO-11A → Derivatisation → HPLC
- Incorporation of aldehydes in online and canister instrumentation for unattended analysis on the same systems as other VOCs

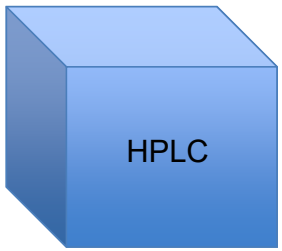
OVOCs:

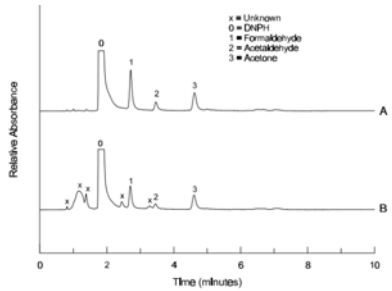
1. Formaldehyde
2. Acetaldehyde
3. Crotonaldehyde
4. Methacrylaldehyde
5. Butyraldehyde
6. Benzaldehyde
7. Pentanal
8. m –Tolualdehyde

Aldehydes



DNPH cartridge





Challenges of the new Chinese regulations

- **Quantitative retention of very volatile to volatile organic compounds in a single analysis**
  - Trapping of the full compound list
  - Fast desorption of all compounds for sharp peaks aiding GC separation
- **Automated unattended analysis**
  - Capacity to run without user intervention
  - Independent check of system performance for every sample with IS addition
- **Water management with no loss of polar compounds**
  - Allows larger sample volumes for maximum sensitivity
  - Protects GC columns and detectors from wear due to water
- **Ability to sample from canister or online**
  - Allows the same instrumentation to be used for on-line or canister samples
- **Trapping and separation of 117 compounds with < 60 minute cycle times**
  - For hourly time-resolution and full data coverage

MARKES international

THE QUEEN'S AWARDS FOR ENTERPRISE: INTERNATIONAL TRADE 2015

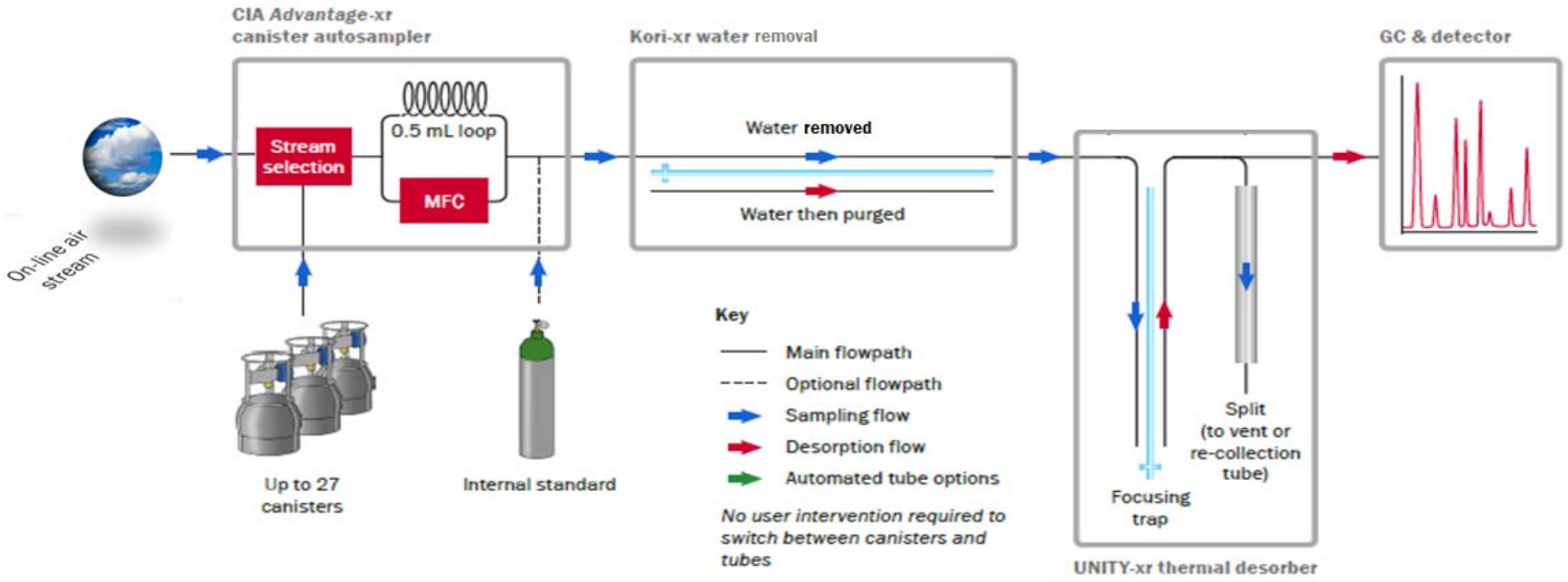
The Solution

Ozone Pre-cursors ✓
Air Toxics ✓
OVOCs ✓

One run – cryogen free ✓

Extending the range of compounds

Setup for tube, online and canister analysis



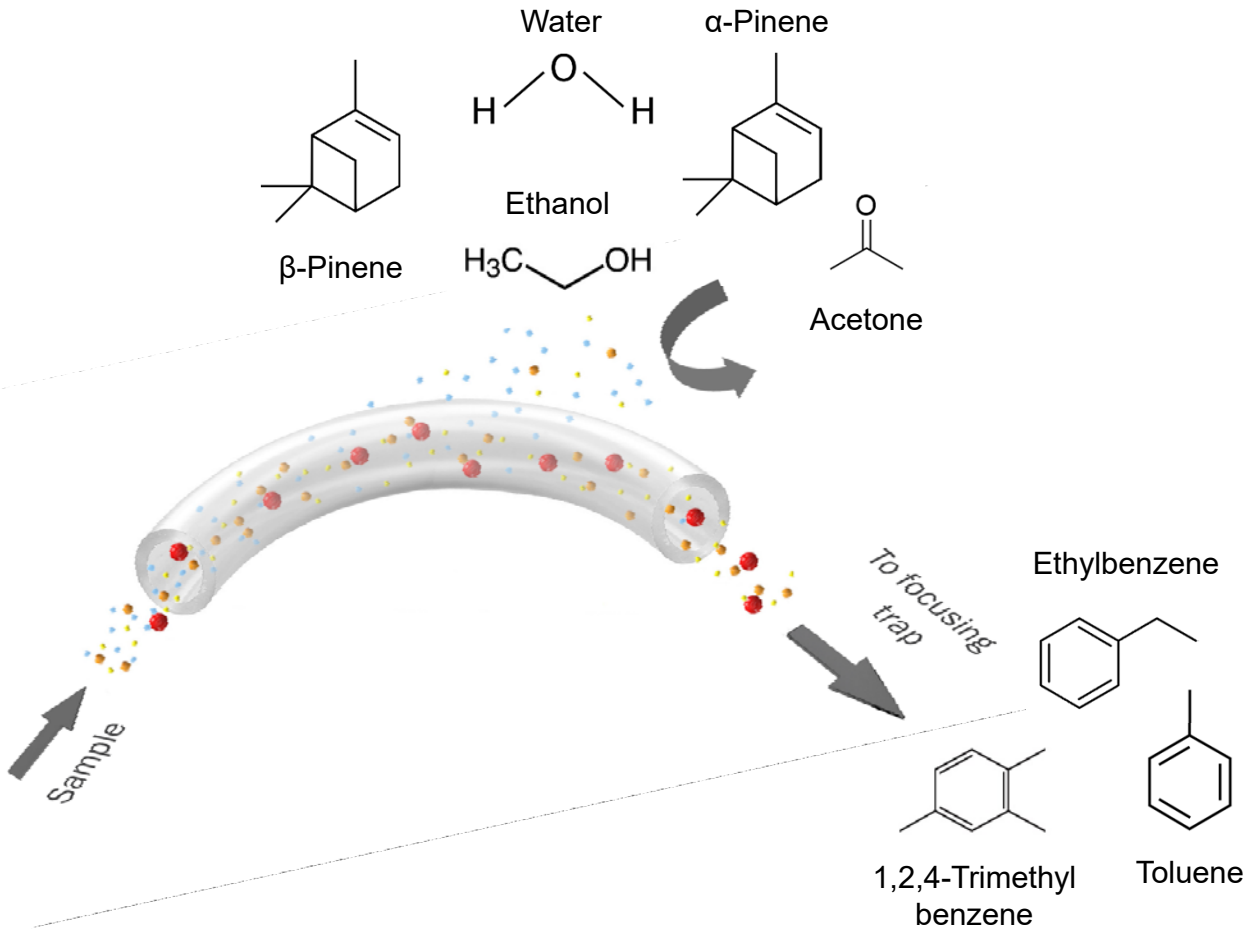
Application note 146

Why is water management a challenge?

Nafion™ dryers

Monoterpenes and polar species that are lost with the water when using Nafion™ dryers.

Compound	Detected using Nafion dryer?
Ethanol	✗
Acetone	✗
Toluene-d_8 (I.S.)	✓
Ethylbenzene	✓
α-Pinene	✗
β-Pinene	✗
1,2,4-Trimethylbenzene	✓

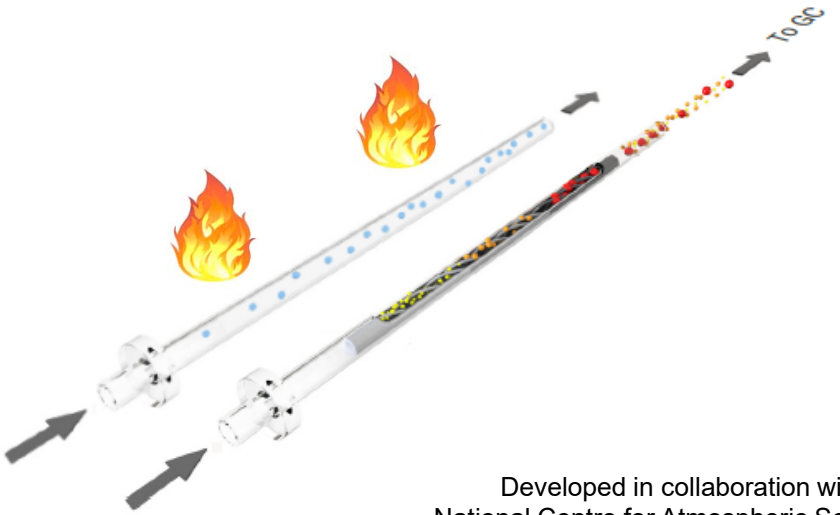


High-performance water removal

Kori-xr

Step 1:
Air sampling and water removal

Step 2:
Trap desorption and water purging



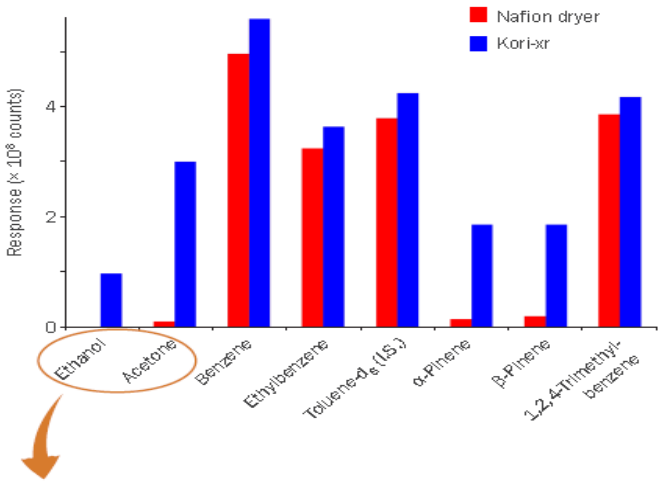
Developed in collaboration with the National Centre for Atmospheric Science (NCAS) at the University of York.

Choosing the right water management approach

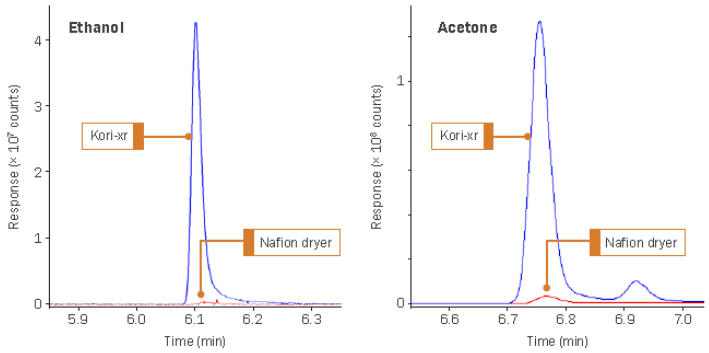
- Monoterpenes and polar species that are lost with the water when using Nafion™ dryers are retained in the sample with Kori-xr.

Compound	Detected using Nafion dryer?	Detected using Kori-xr?
Ethanol	✗	✓
Acetone	✗	✓
Toluene-d_8 (I.S.)	✓	✓
Ethylbenzene	✓	✓
α-Pinene	✗	✓
β-Pinene	✗	✓
1,2,4-Trimethylbenzene	✓	✓

Comparison carried out using air at 80% relative humidity



Strong responses from highly polar compounds



MARKES international

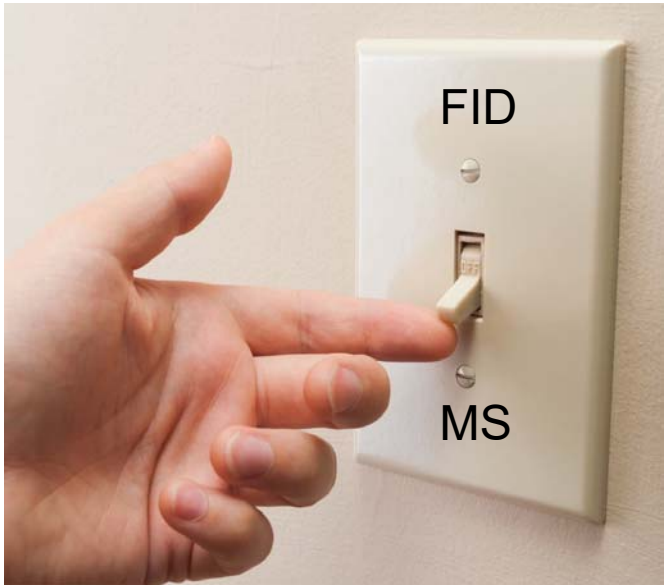
MS & FID detection with Deans switch

Why?

The large range in volatility in the complex target list calls for:

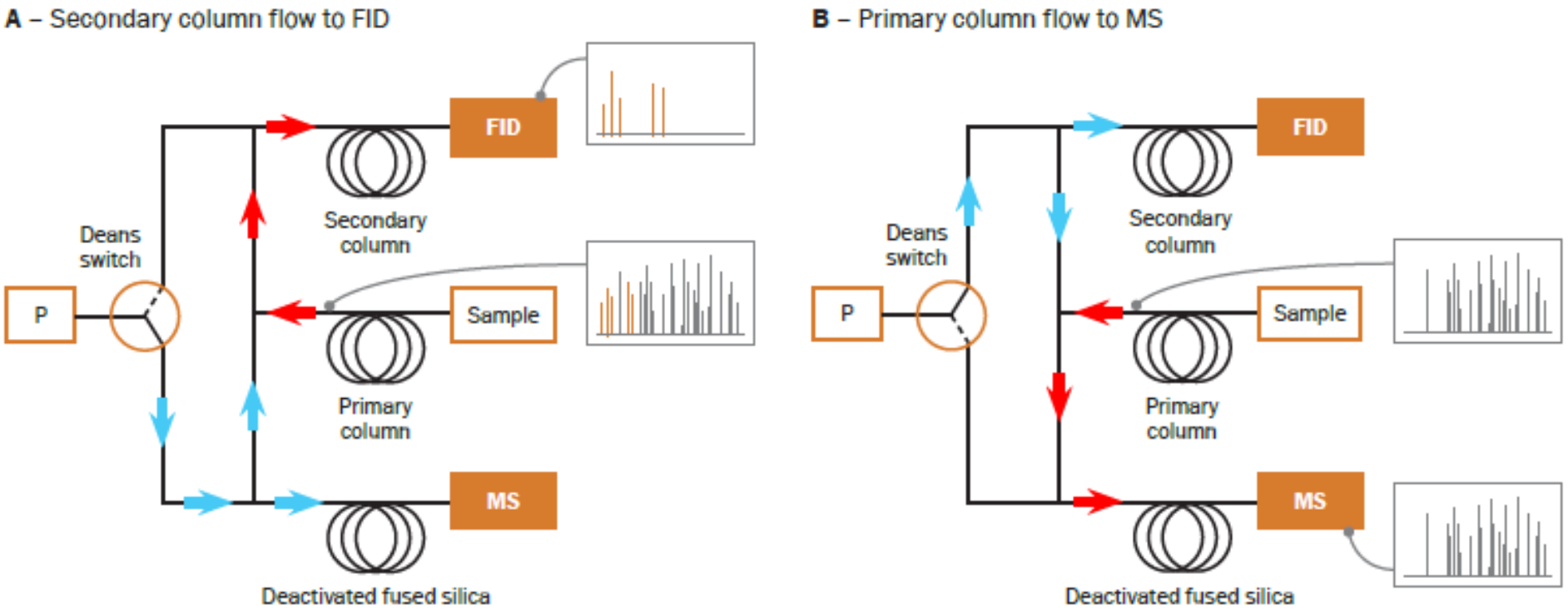
- Separation on highly retentive columns
- Consideration of what detector will be most suitable for each compound

Use the best of both detectors to minimise analytical time and achieve best possible MDLs



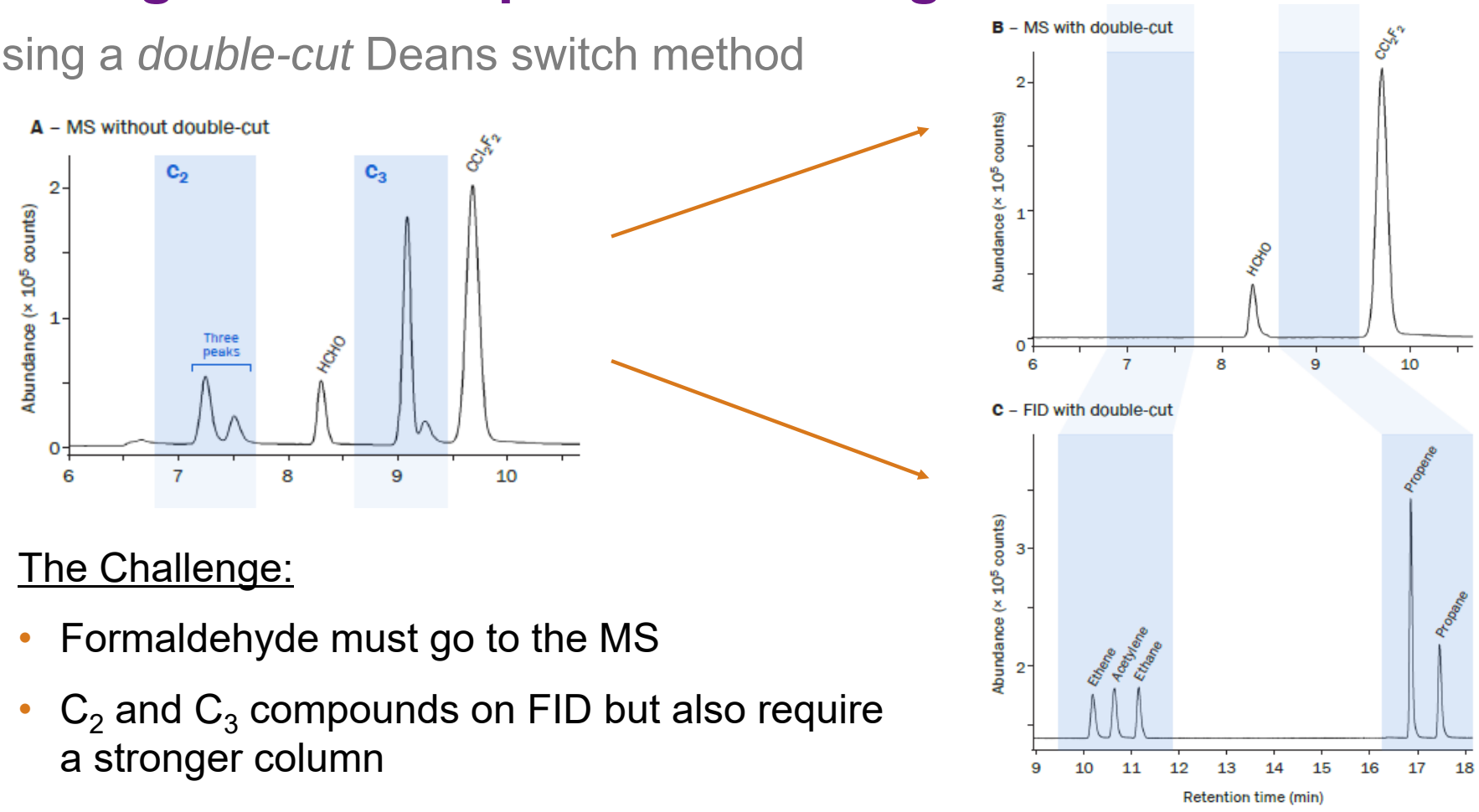
Optimum sensitivity together with excellent peak shape

Deans switch method



Getting the best separation and right detector

Using a *double-cut* Deans switch method



<u>The Challenge:</u>

- Formaldehyde must go to the MS
- C_2 and C_3 compounds on FID but also require a stronger column

MARKES international

MARKES international

THE QUEEN'S AWARDS FOR ENTERPRISE: INTERNATIONAL TRADE 2015

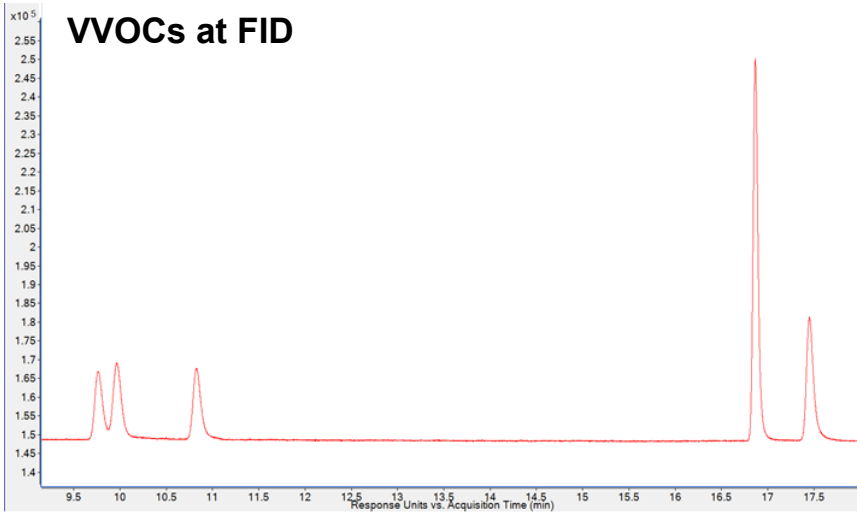
The Results

117 compounds at any humidity in under 1 hour

Results

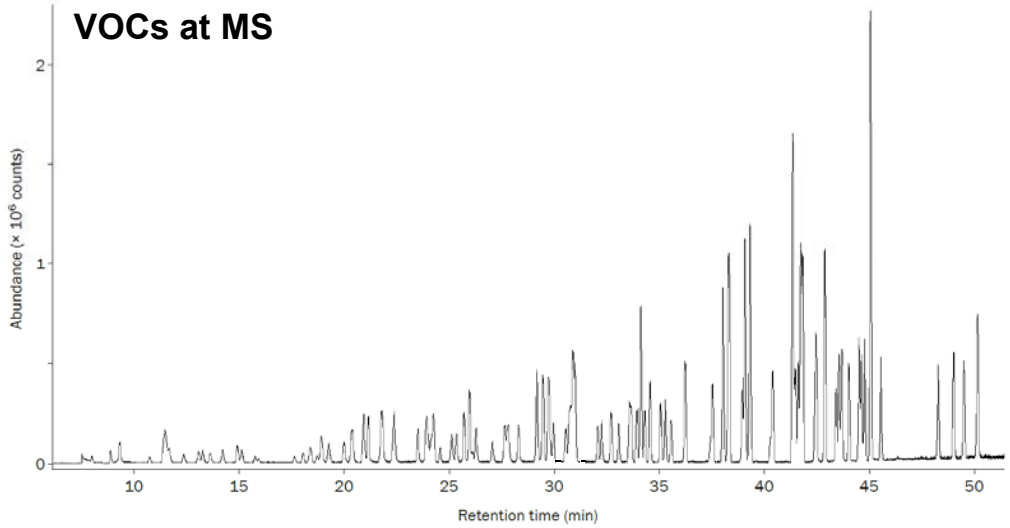
PAMs, TO-15 & OVOC in a single analysis with no liquid cryogen

VVOCs at FID



5 compounds

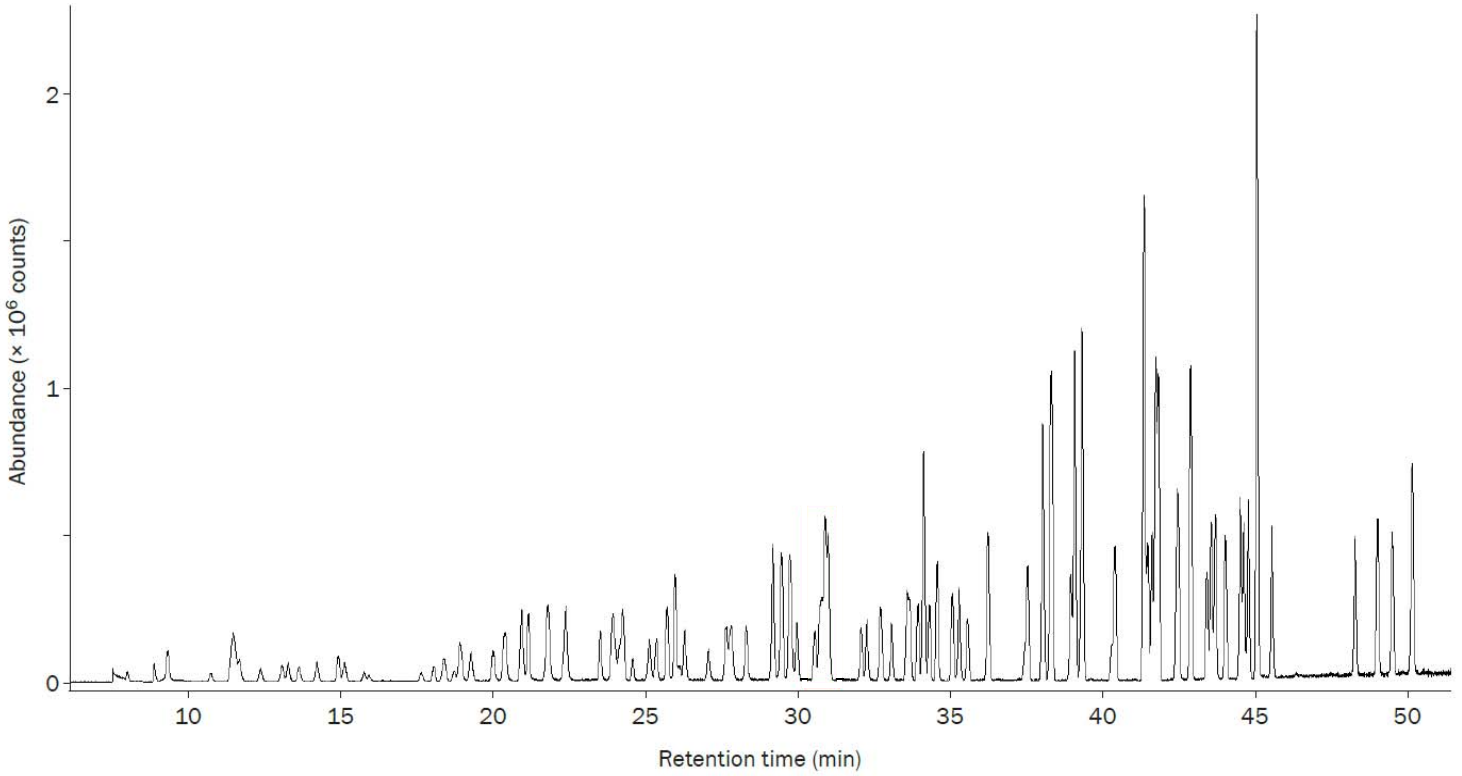
VOCs at MS



112 compounds

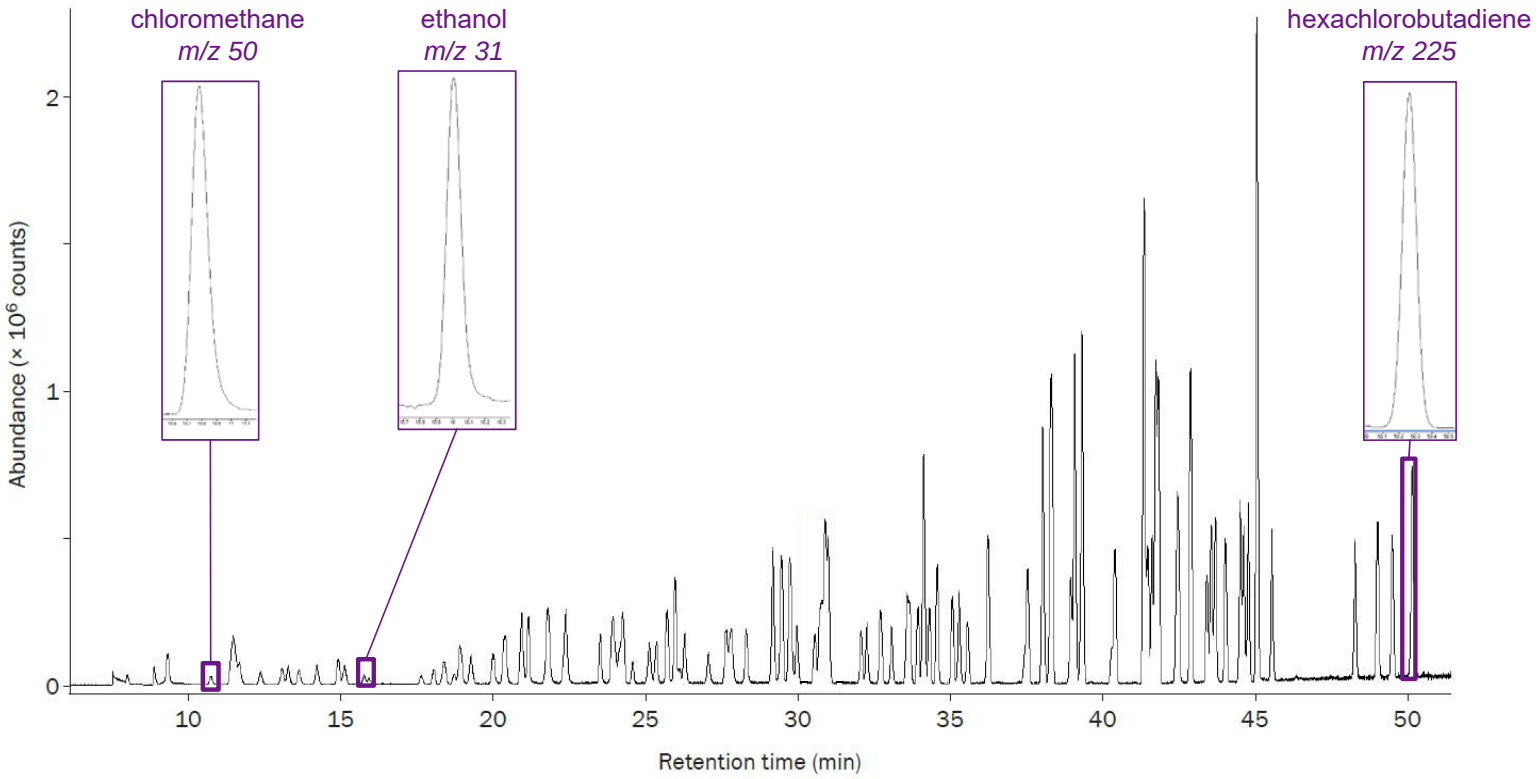
Results

PAMs, TO-15 & OVOC in a single analysis with no liquid cryogen



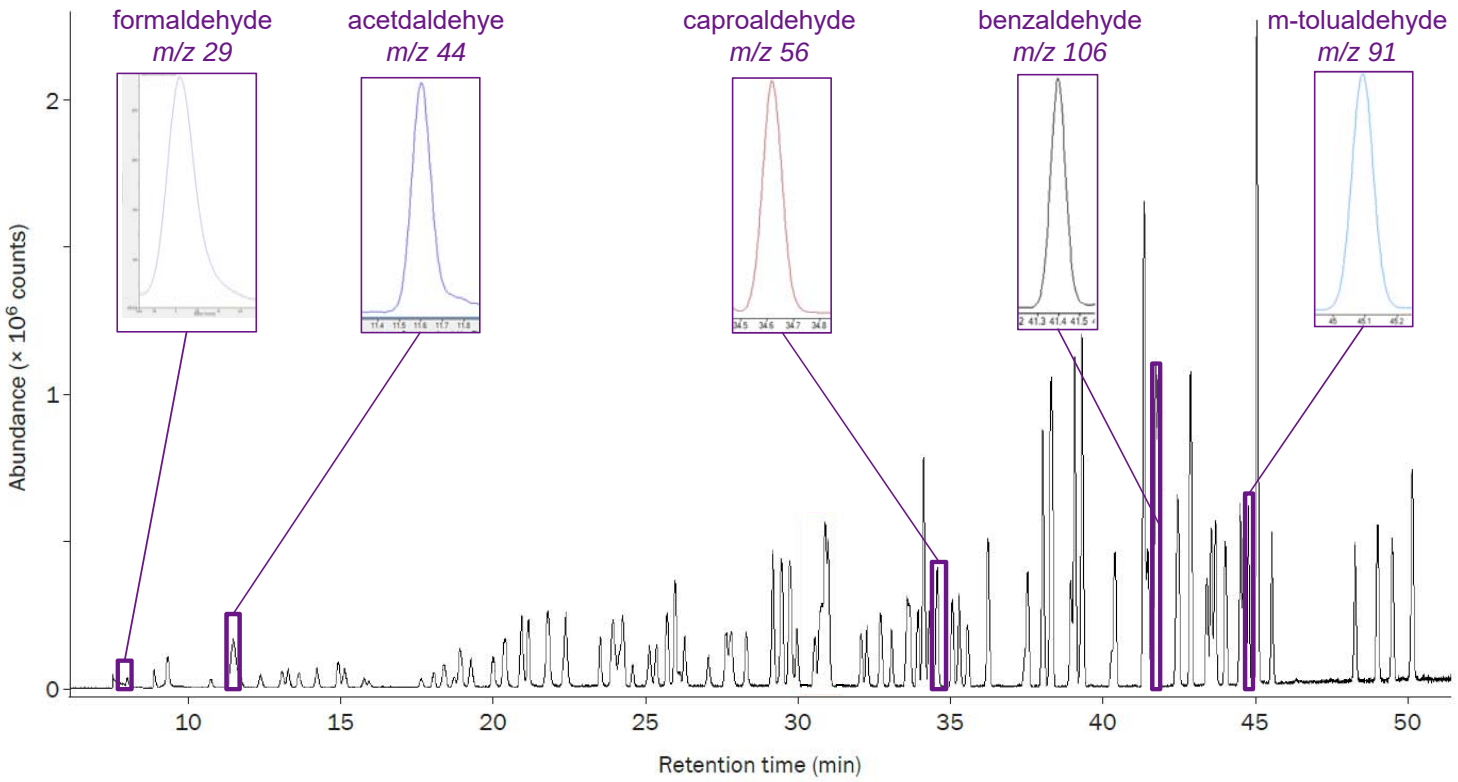
Results

PAMs, TO-15 & OVOC in a single analysis with no liquid cryogen



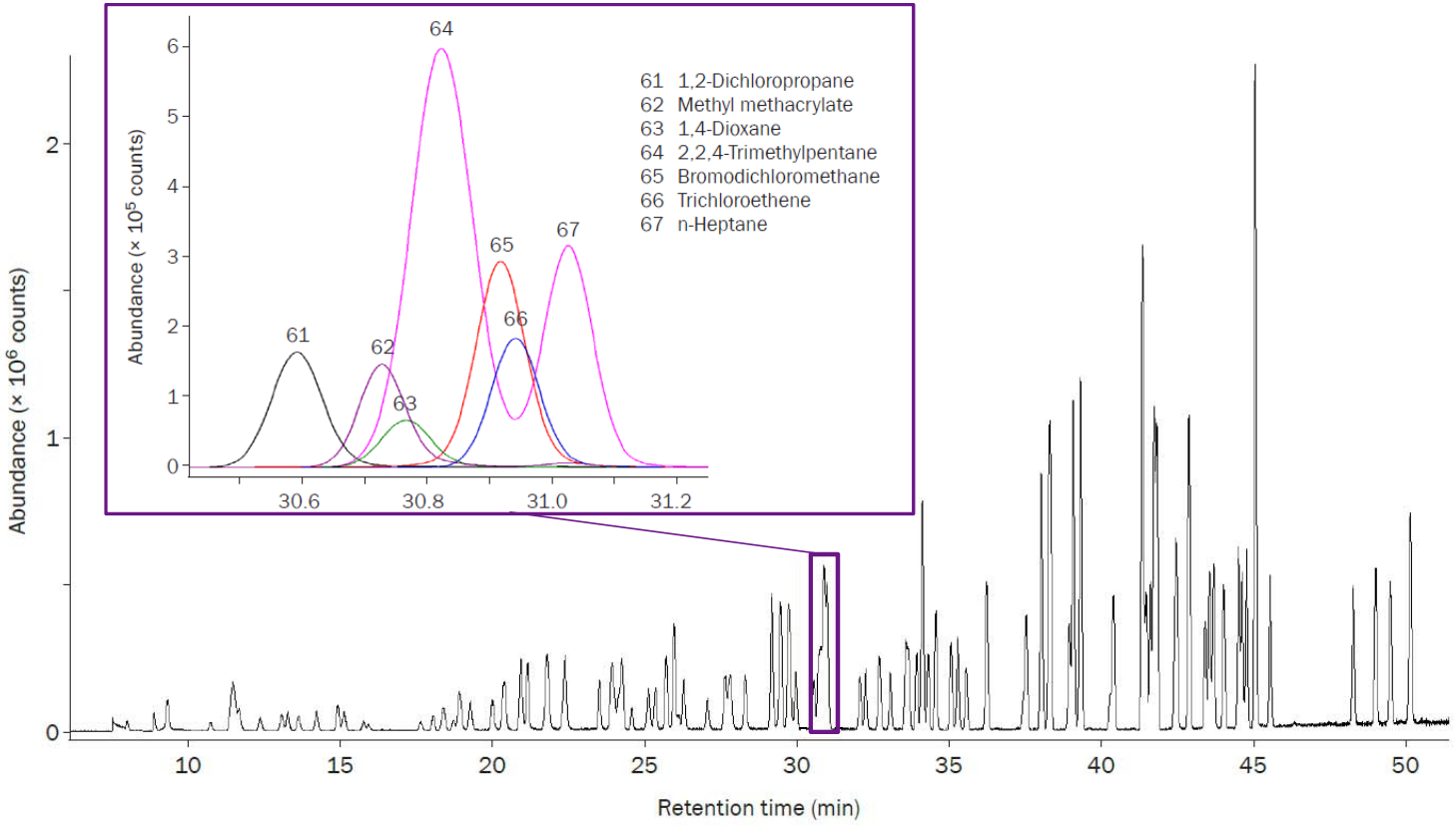
Results

PAMs, TO-15 & OVOC in a single analysis with no liquid cryogen



Results

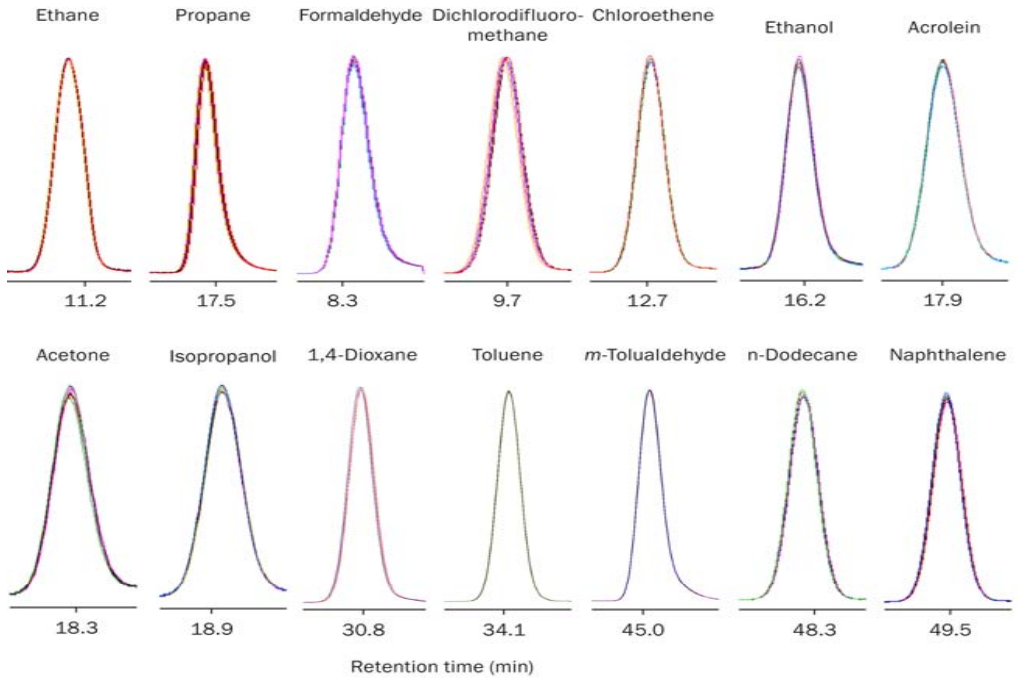
PAMs, TO-15 & OVOC in a single analysis with no liquid cryogen



Reproducible unattended analysis

Excellent retention time stability

- Highly reproducible data:
  - < 7.5% RSD on response across 10 replicates for all compounds
  - < 2.1% RSD for internal standard compounds
- Very stable retention times:
  - < 0.17% RSD across 16 replicates for all compounds



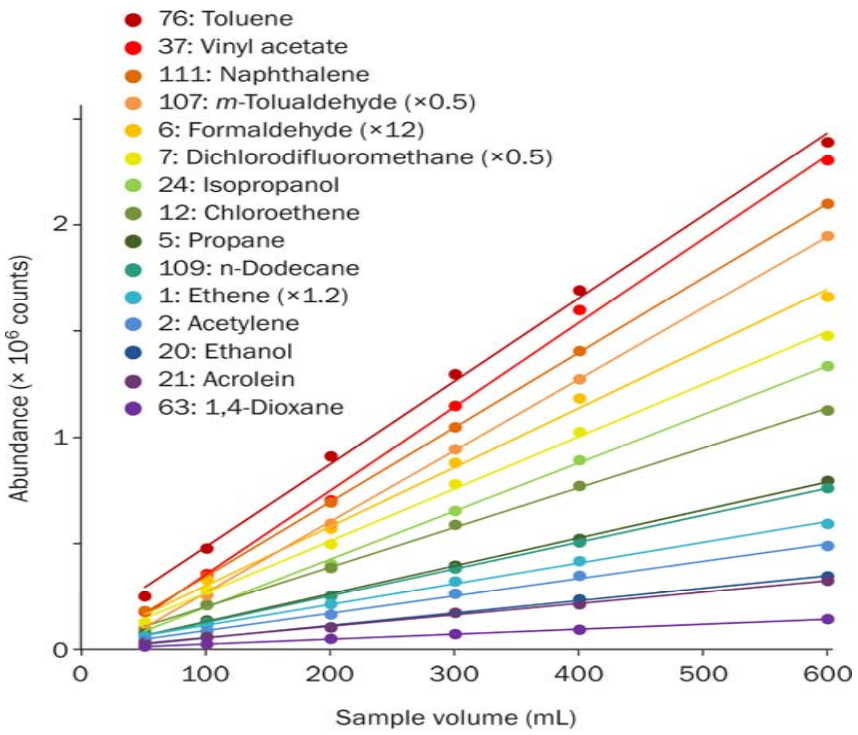
Example compounds covering the polarity and volatility range of the target list:
10 replicate analysis of 10 ppb standard at 100% RH overlay perfectly for all compounds

Great linearity and low detection limits

…at 100% relative humidity!

Excellent linearity at 100% relative humidity

- 1.25 to 15 ppb equivalent
- All R^2 values > 0.990
- Relative response factors highly reproducible
- % RSD of RRF ≤ 12% (method limit 30%)



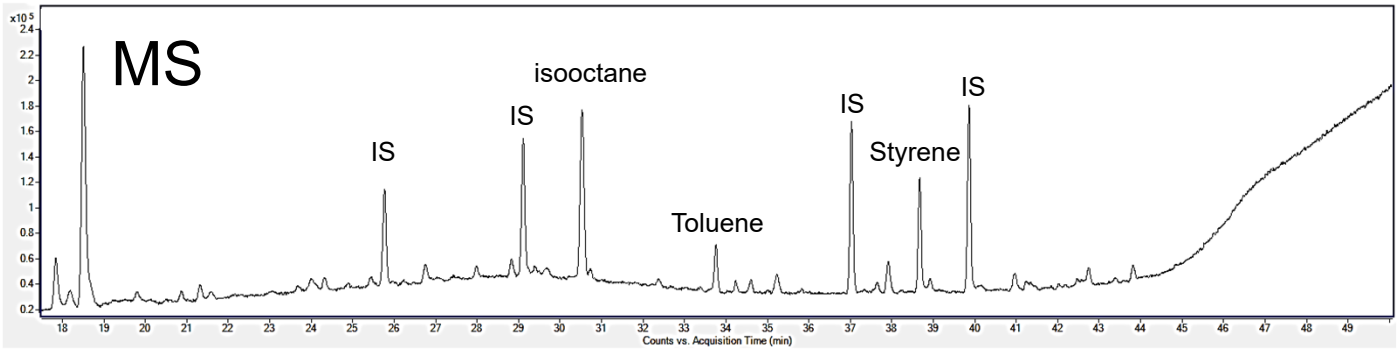
Low method detection limits

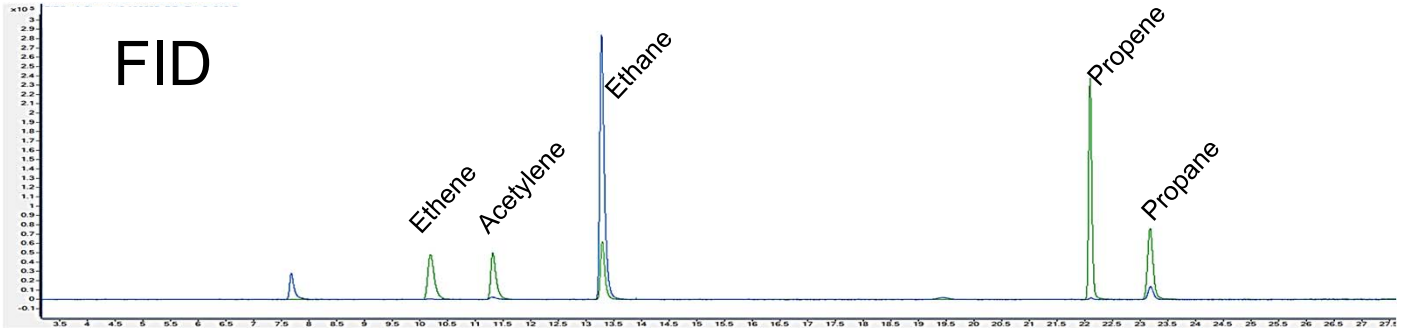
- All MDLs < 200 ppt
- Average MDL ~ 50 ppt

Compounds	MDL (ppt)
Toluene	8
Vinyl acetate	72
Naphthalene	26
m-Tolualdehdye	70
Formaldehyde	105
Dichlorodifluoro methane	22
Isopropanol	114
Chloroethene	47
Propane	22
N-Dodecane	73
Ethene	92
Acetylene	99
Ethanol	43
1,4-Dioxane	120

Real Air Sample

TO-15, PAMS and OVOCs in Welsh Air



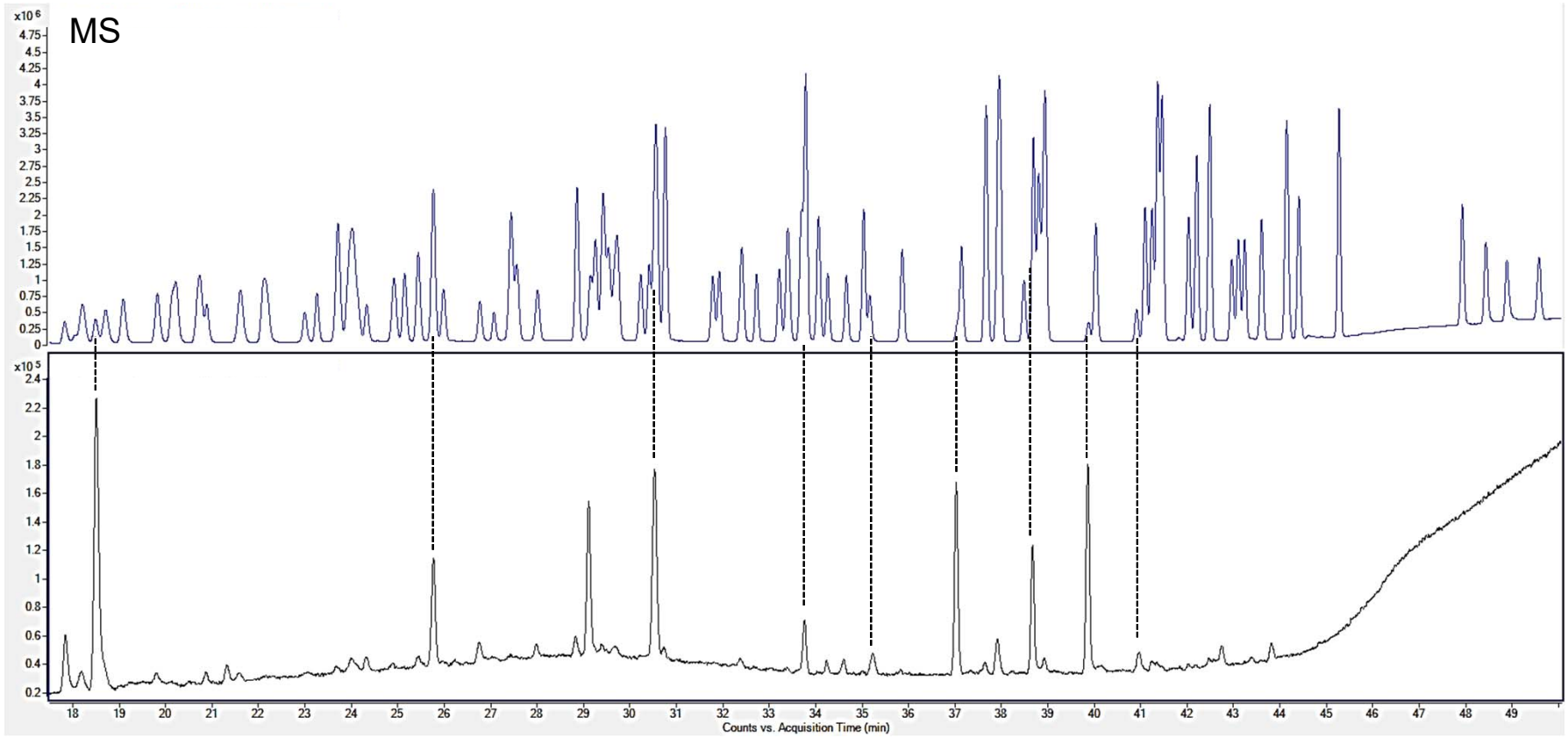


Brecon Beacons

MARKES international

Excellent retention time stability

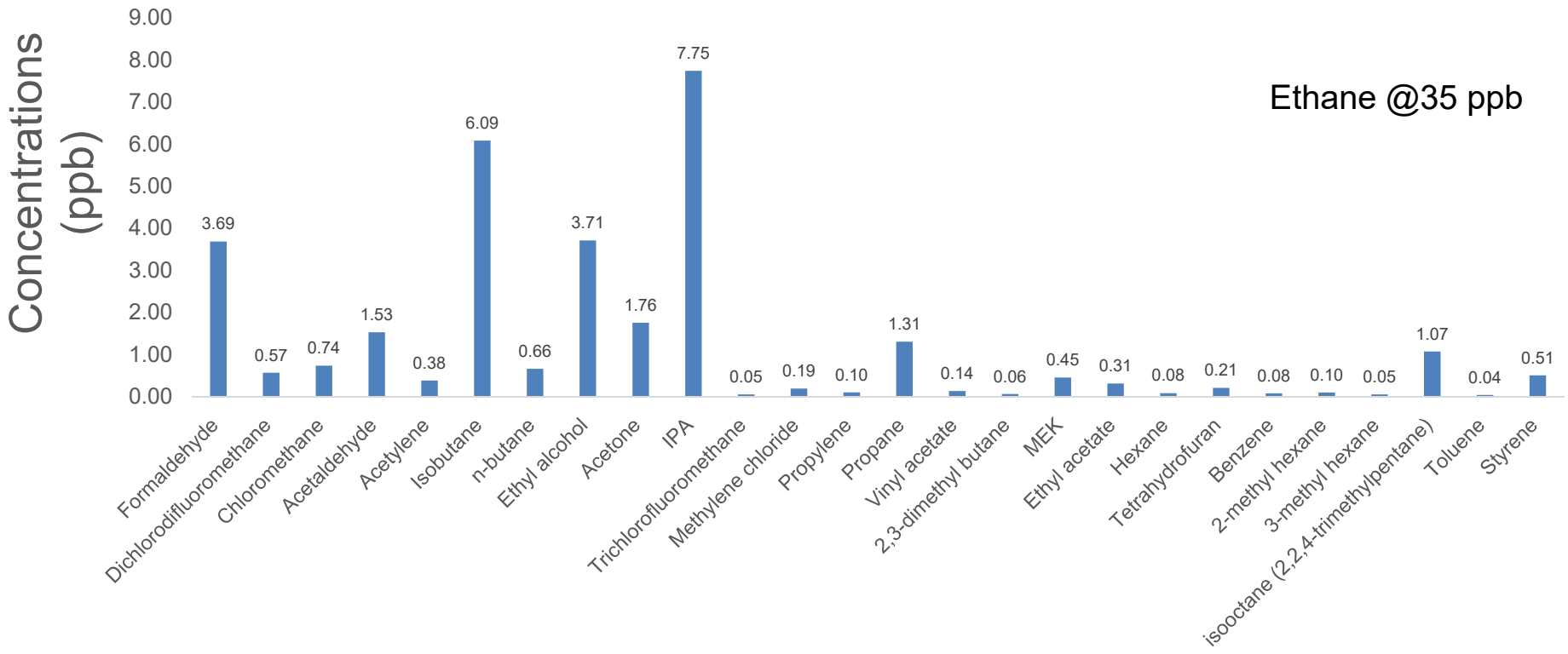
TO-15, PAMS and OVOCs in Welsh Air



MARKES international

What do the Welsh breathe?

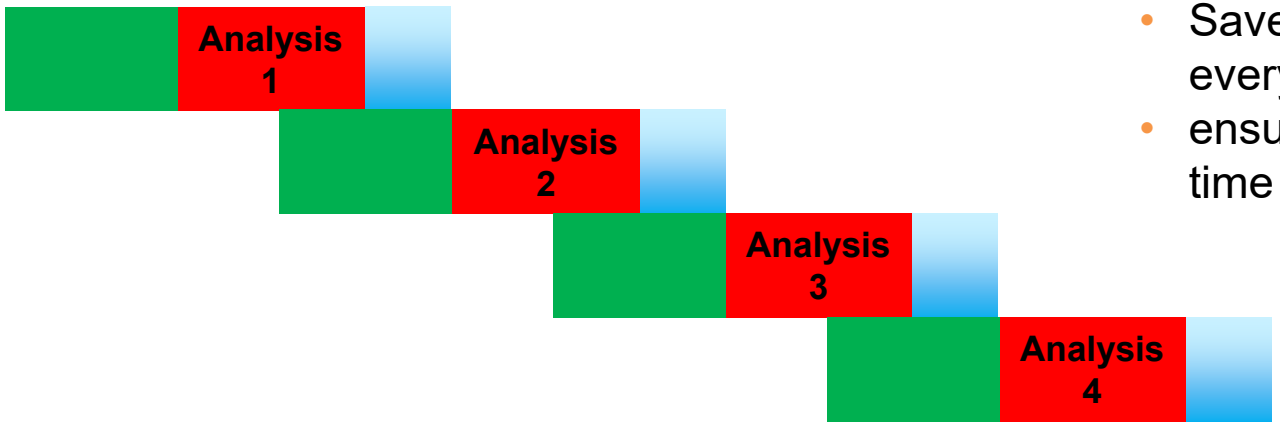
Concentrations at midnight



Maximising productivity with CIA Advantage-xr

Overlap mode

- Allows the focusing of a subsequent sample to begin during the GC analysis of the previous sample.
- The sample is loaded on the cold trap and ready to be analysed as soon as the GC has cooled from the previous run, maximising lab throughput.



- Saves an hour for every three runs
- ensures >1h cycle time

Successful PAMS, TO-15 & OVOC analysis requires….

- Quantitative retention of very volatile to volatile organic compounds in a single analysis
- Automated unattended analysis
- Water management with no loss of polar compounds
- Ability to sample from canister or online
- Trapping and separation of 117 compounds with < 60 minute cycle times

Achieve all this *and more* with Markes thermal desorption systems!

MARKES international

Since 1997 20 YEARS ANNIVERSARY

Contact Markes


enquiries@markes.com


+44 (0)1443 230935


www.markes.com


@MarkesInt


www.linkedin.com/company/markes-international