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THE QUEEN'S AWARDS FOR ENTERPRISE: INNOVATION 2019

Beyond TO-15

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A company of the SCHAUENBURG International Group

Introduction

TO-15 Dominated Air Monitoring for 20 Years

- Superseded by TO-15a in 2020
- Influences global standards
- Evolved into more analytically challenging methods
  - Complex target lists
  - Ever decreasing limits of detection
  - High throughput methods
  - Reduced cost per analysis

TO-15 type workflow

Canisters and sample train are:

- Cleaned
- Checked
- Evacuated

Sampling

- Grab sample
- Time Weighted Average (TWA) sample

Analysis

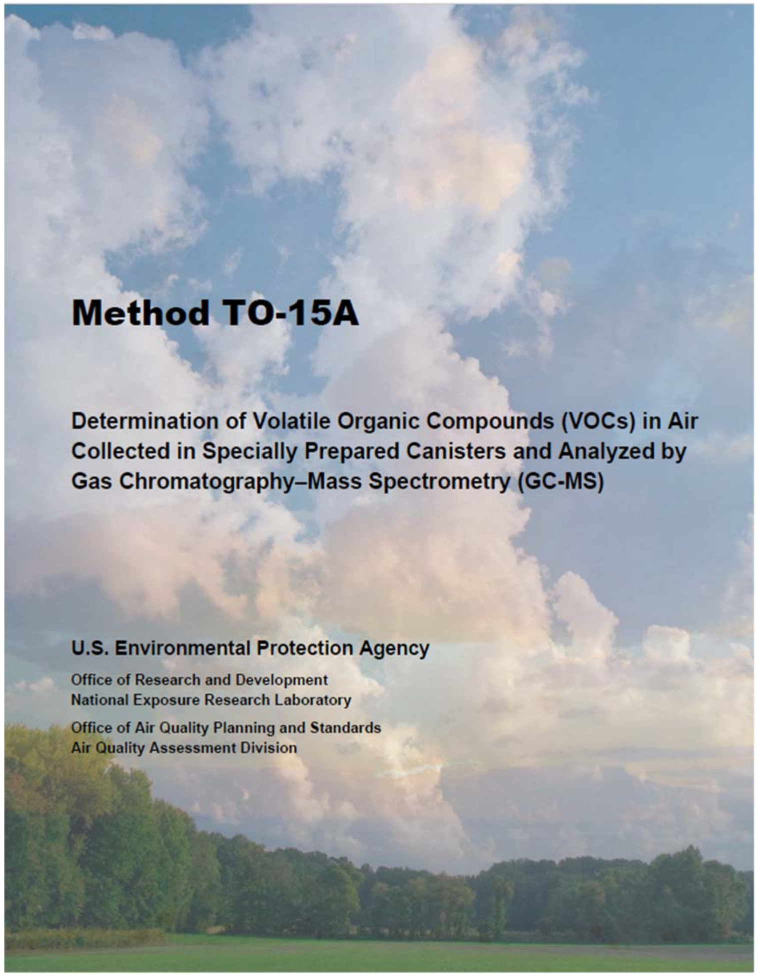
- Criteria based
- Calibration
- Internal standard
- Scan or SIM

What has changed in TO-15a?

And how does that affect instrumentation?

- The method is much more in depth.
- Great resource for those just starting out in canister analysis
- Thorough instruction on many parts of sampling and analysis

1. MDLs have dropped to 20pptv
2. Water management techniques are now included



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MDLs have dropped to the range of 20pptv

What does this affect?

Sample volume

- Larger volumes than labs are taking currently may be required
- Water management may be required if volumes increase
- Instruments which can't sample more than 400mL may not be suitable for the analysis

Detector technology

- Older MS instruments currently being used may not be able to get down to these levels
- SIM/Scan, TOF technology is now included as a suggested instrument type

Cleanliness

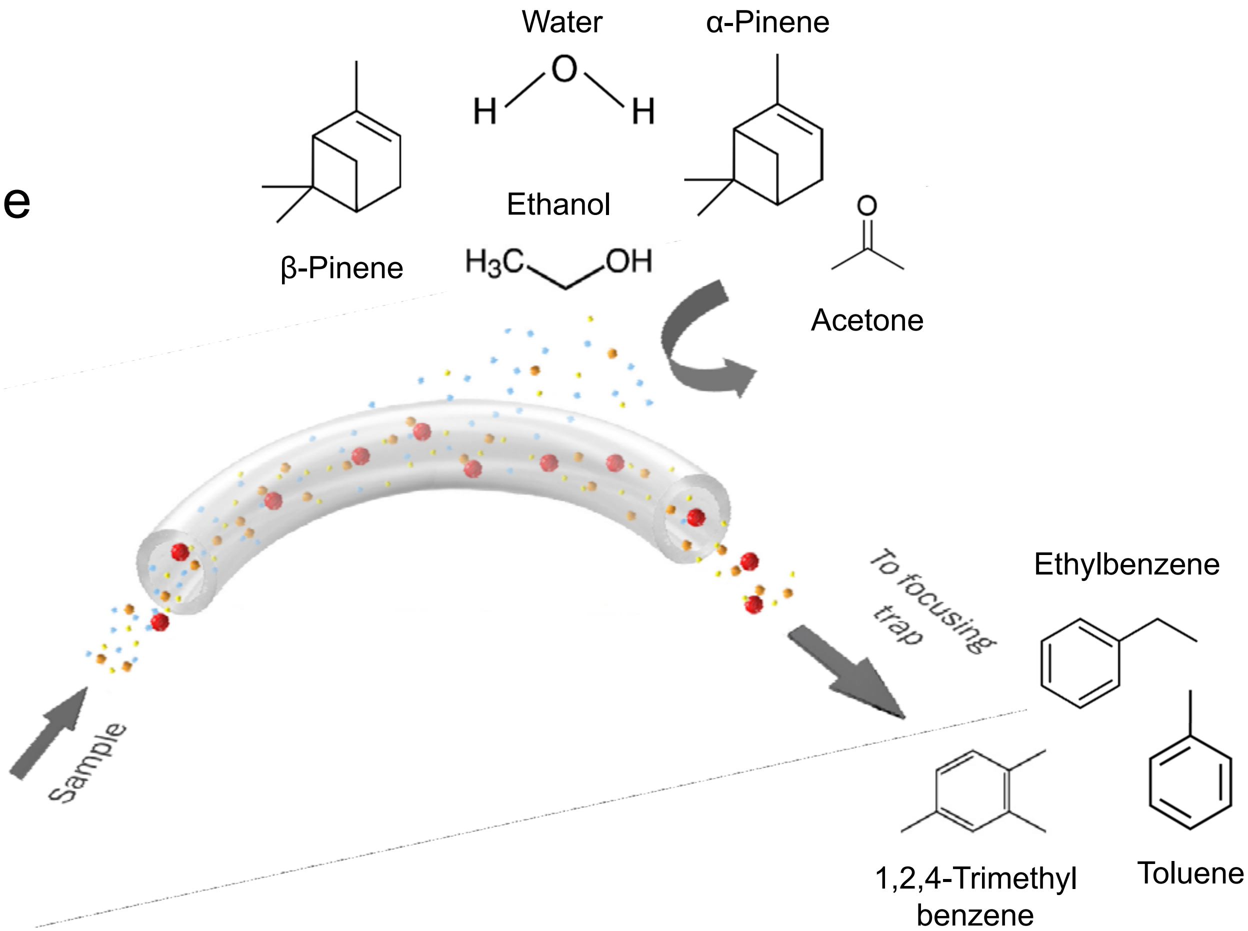
- Spec for both instrumentation and canisters is now also 20pptv or below
- The biggest challenge the EPA saw from this change was the processes surrounding canister cleaning

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	✓



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High-Performance Water Removal

Water Abstraction Device – 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.

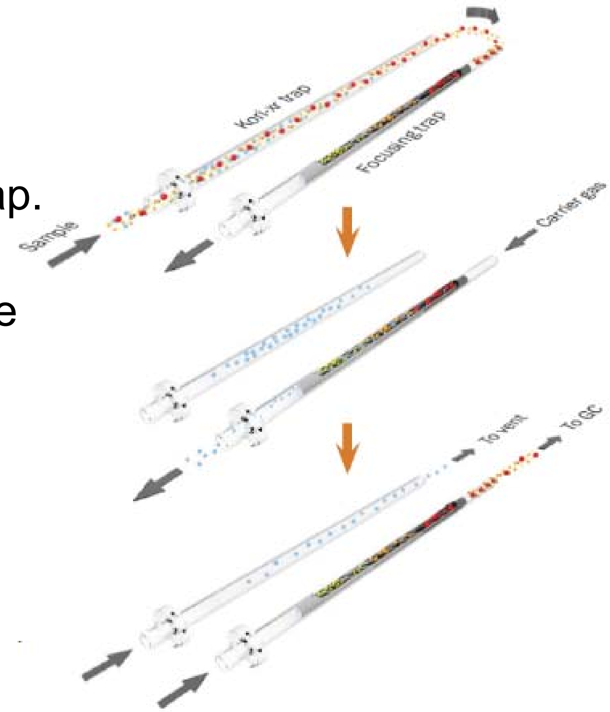
Unique Dry-Focus3 mechanism

Remove – Focus – Dry

Dry-Focus3 harnesses the power of Kori-xr and UNITY-xr in a 3-stage operation to deliver optimum drying efficiency, sensitivity and selectivity.

Three fully-automated stages of operation:

1. **Sampling**
   Removal of bulk airborne humidity using trap in Kori-xr whilst collecting targets on electrically cooled focusing trap.
2. **Trap purge**
   Dry purge the focusing trap at programmable temperature (-30 to 50°C) to remove any residual water.
3. **Desorption**
   Focusing trap rapidly heated in reverse flow to inject analytes into GC column. Simultaneously, the isolated water in the Kori-xr trap is purged to vent, ready for the next sample.



Water management techniques are now included

How does it help?

Lower detection limits

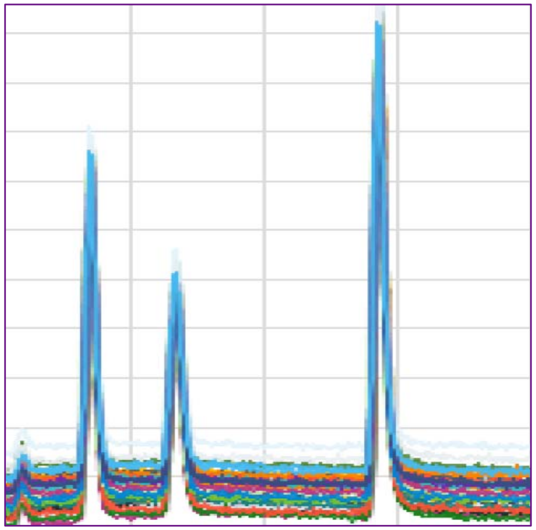
- Larger sample volumes can be taken without concern for water interference

Confidence in results

- Stabilised retention times
- Reduced water interference

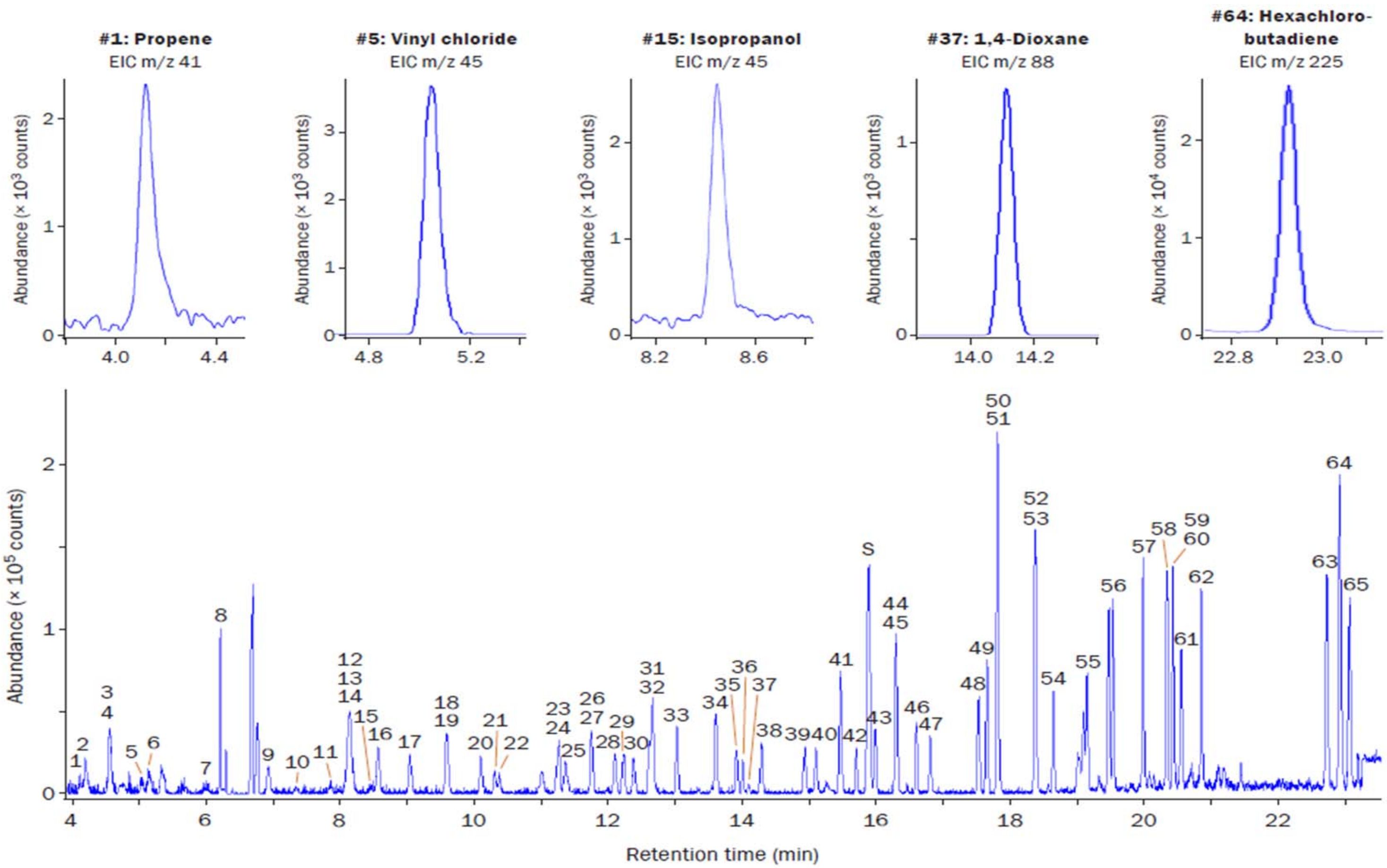
Less instrument downtime

- Column lifetimes extended
- More time between cleaning MS



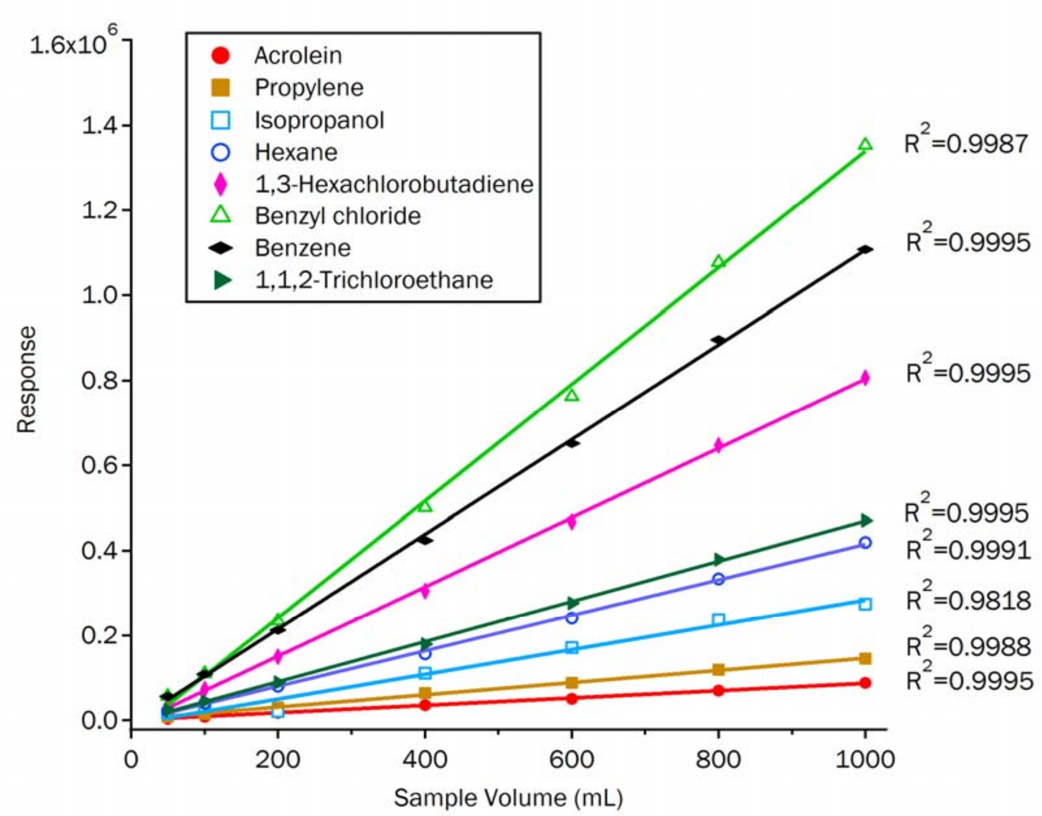
38 repeats over 1 month with CIA Advantage and Kori-xr

Peak shape and productivity



- Profile shows excellent transfer through the system
- Great peak shape
- Fast turn around – all compounds in under 25 minutes

Linearity and MDLs



Compound	MDL in SIM
Propene	5 ppt
Vinyl Chloride	1 ppt
Carbon disulfide	2 ppt
1,4 – Dioxane	5 ppt
Toluene	3 ppt
Styrene	2 ppt
Hexachlorobutadiene	2 ppt

The newest challenge in air monitoring

Ozone Precursors
Smog forming compounds

Very volatile, non-polar C_2-C_{12} hydrocarbons.

e.g US EPA PAMS

Air Toxics
Hazardous air pollutants

Polar, non-polar and halogenated compounds

e.g US EPA TO-15

OVOCs
Oxygenated VOCs

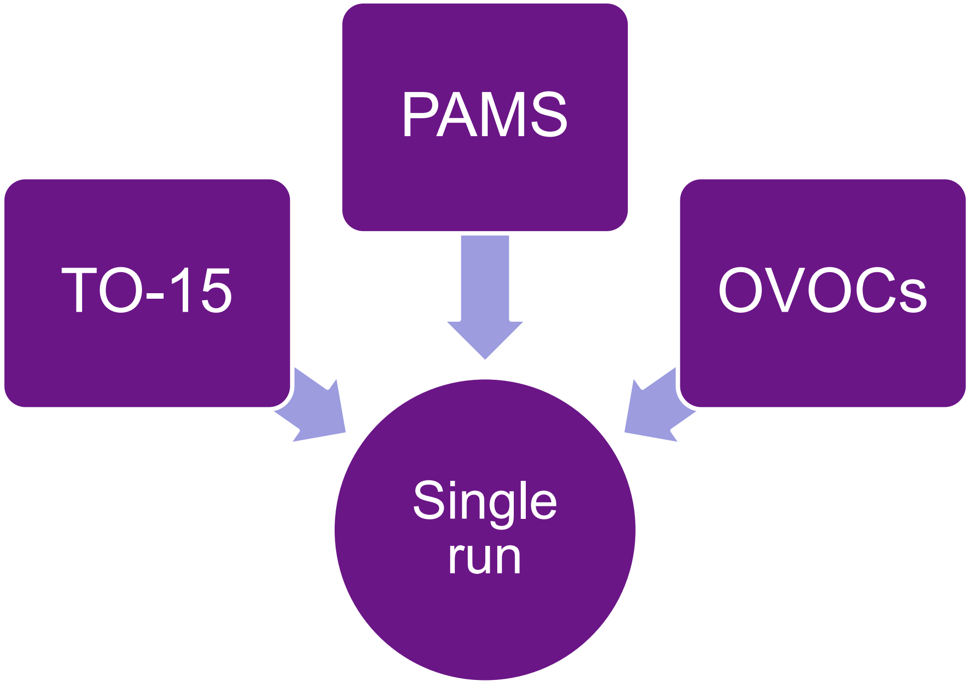
Aldehydes and ketones e.g formaldehyde.

e.g US EPA TO-11A

The newest challenge in air monitoring

Obtaining double the data in the same amount of time

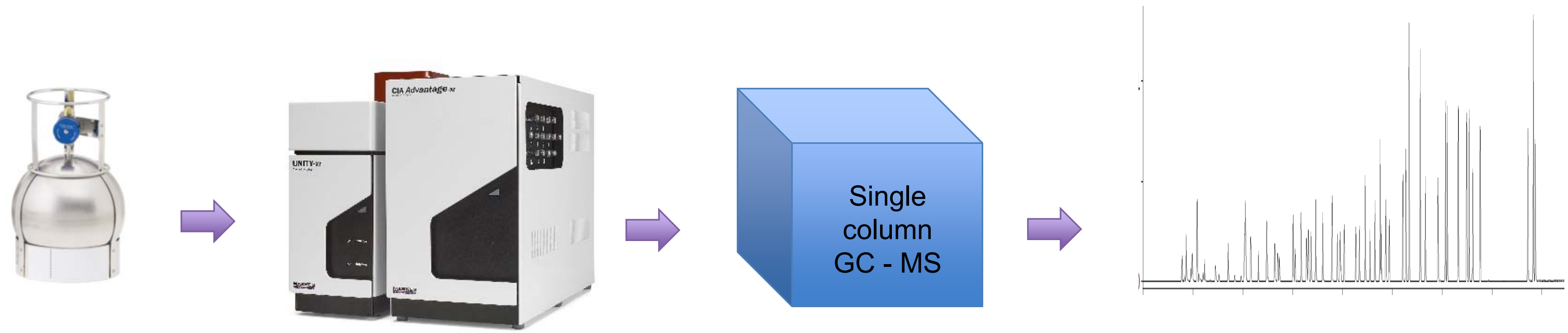
- Combining 3 target lists
- Total of 117 compounds in 1 hour
- Mandatory in China but of growing interest worldwide
- Integrating the analysis of formaldehyde by TD-GC-MS, without derivatisation



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



From C_3

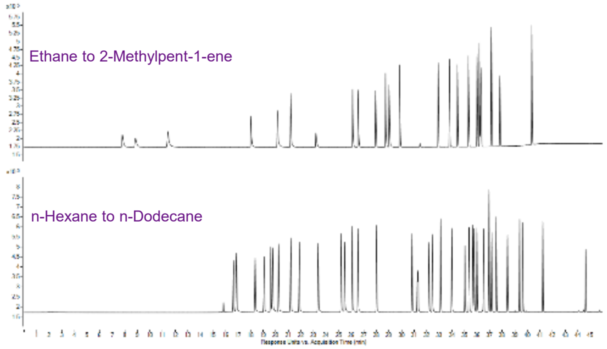
PAMS

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 a Nafion dryer can't be used.

C_2-C_{12}

Dual column GC - FID



OVOCs

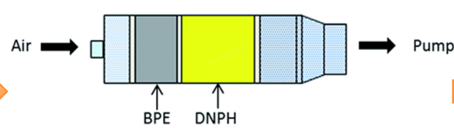
Oxygenated volatile organic compounds

- 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

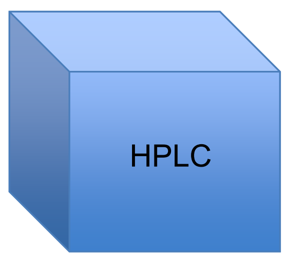
OVOCs:

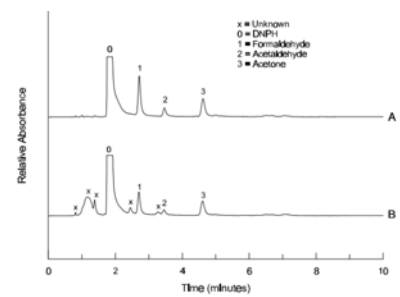
1. Formaldehyde
2. Acetaldehyde
3. Crotonaldehyde
4. Methacrylaldehyde
5. Butyraldehyde
6. Benzaldehyde
7. Pentanal
8. m –Tolualdehyde

Aldehydes



DNPH cartridge



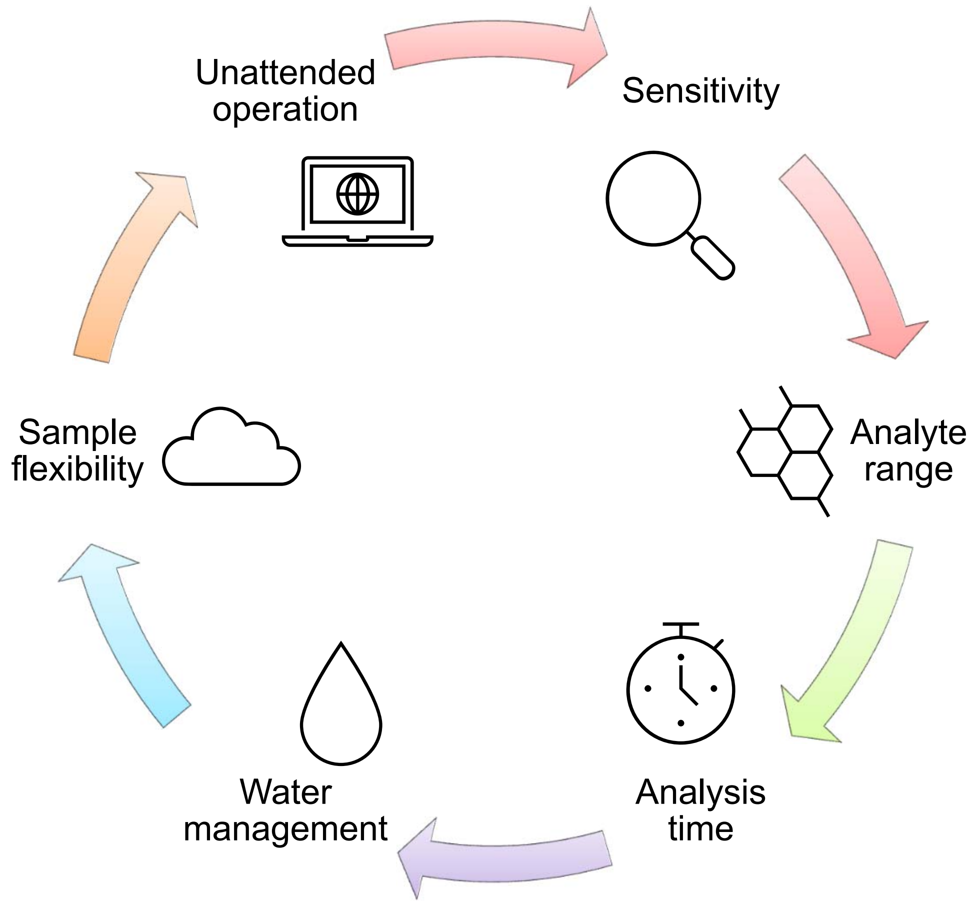


Challenges of analyzing 117 compounds

- 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

Challenges of analyzing 117 compounds

- 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



Why is this methodology of interest globally?

Complexity of the requirement

- No cryogen used
- C_2 to Naphthalene – difficult chromatographically
- The range of chemical classes included
  - Hydrocarbons
  - Halogenated
  - Alcohols
  - Aldehydes
  - Ketones
  - Dioxane
  - Aromatics and PAHs

Formaldehyde

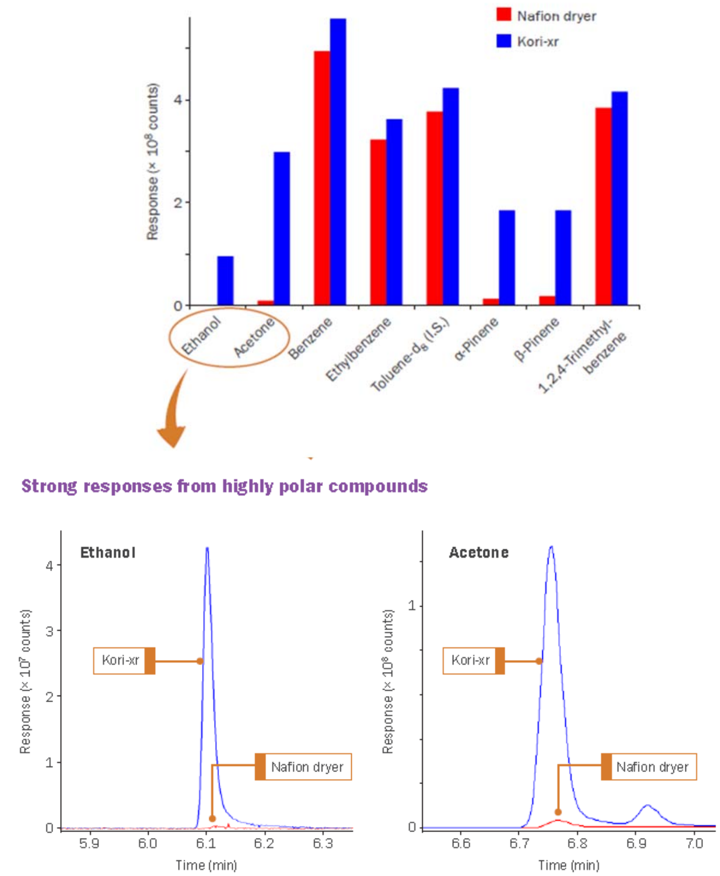
- Ambient air
- Indoor Air
- Vehicle interior air

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.

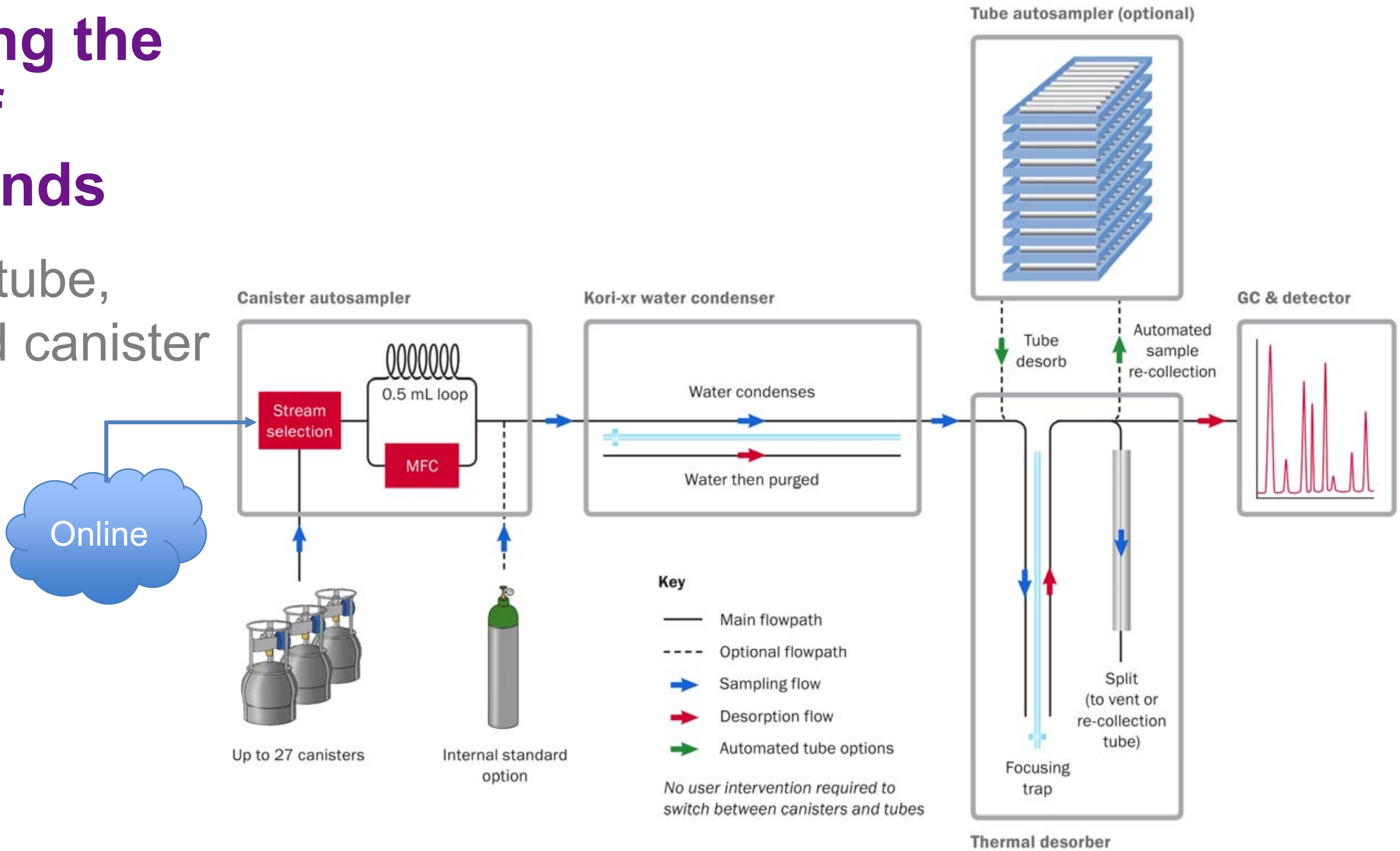
Compound	Detected using Nafion dryer?	Detected using Kori-xr?	Response linearity (R^2) using Kori-xr
Ethanol	✗	✓	0.973
Acetone	✓	✓	0.993
Toluene-d_8 (I.S.)	✓	✓	1.000
Ethylbenzene	✓	✓	0.999
α-Pinene	✗	✓	0.999
β-Pinene	✗	✓	0.997
1,2,4-Trimethylbenzene	✓	✓	0.999

Comparison carried out using air at 80% relative humidity



Extending the range of compounds

Setup for tube, online and canister analysis



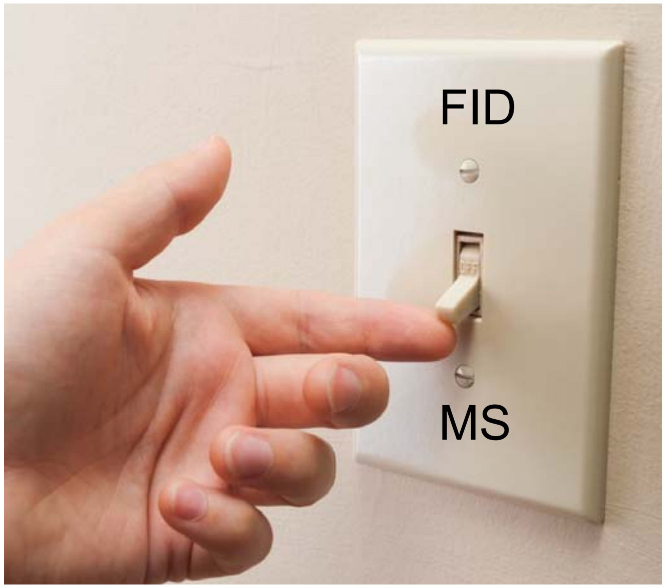
MS & FID detection with Deans switch

Why?

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

- Separation on highly retentive columns
  - PLOT columns provide the best separation of the Ultra volatile PAMS species
- Consideration of what detector will be most suitable for each compound
  - Whilst it is very volatile formaldehyde cannot be detected sufficiently using FID detectors

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

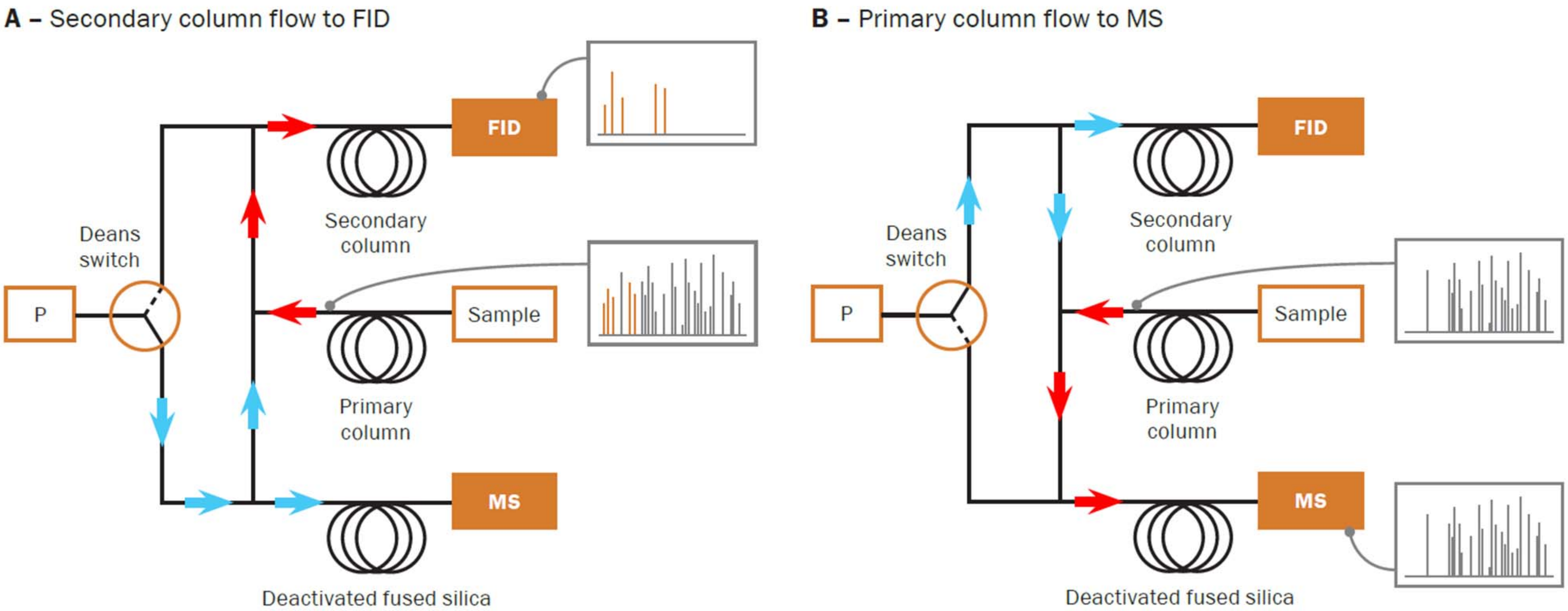
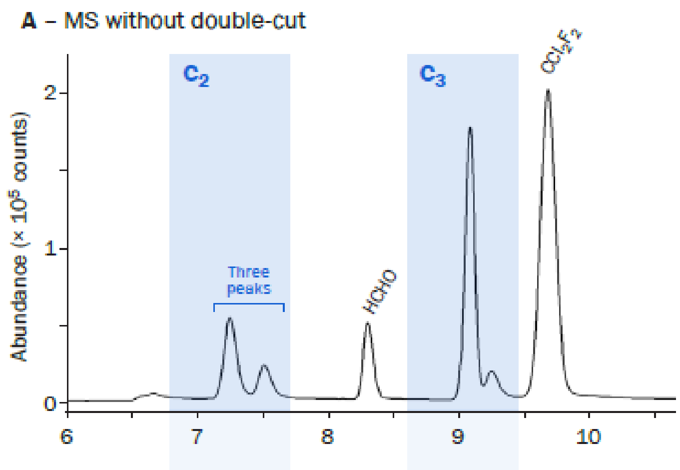
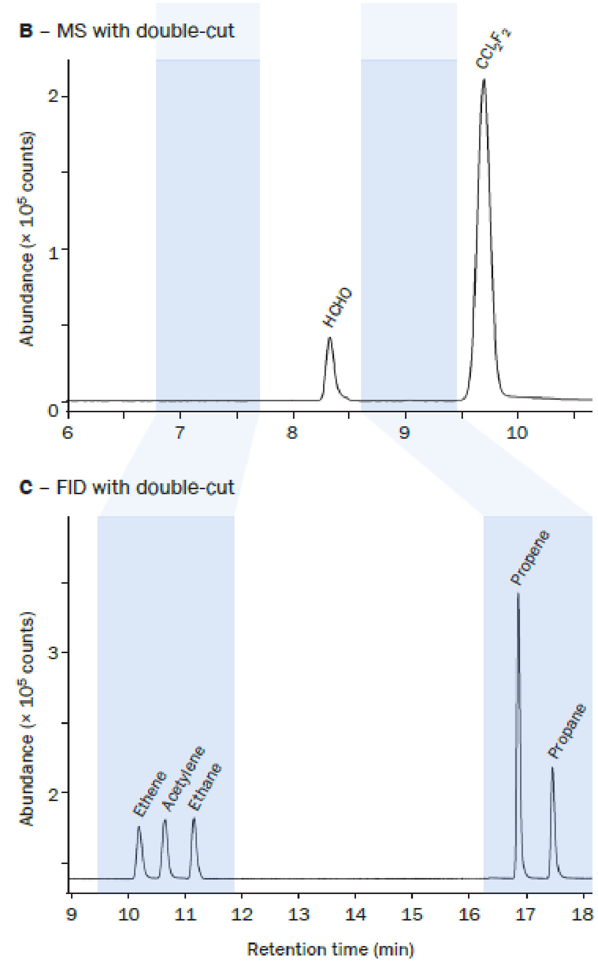


Figure 4: Dual-column GC–MS/FID instrument operation. = Analyte flow. = Gas flow. P = Carrier gas pressure supply.

Getting the best separation and right detector

Using a *double-cut* Deans switch method



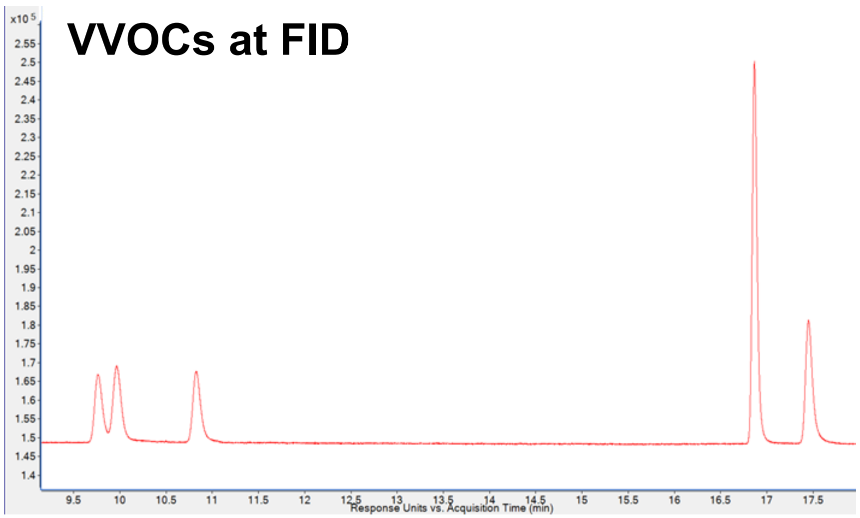


<u>The Challenge:</u>

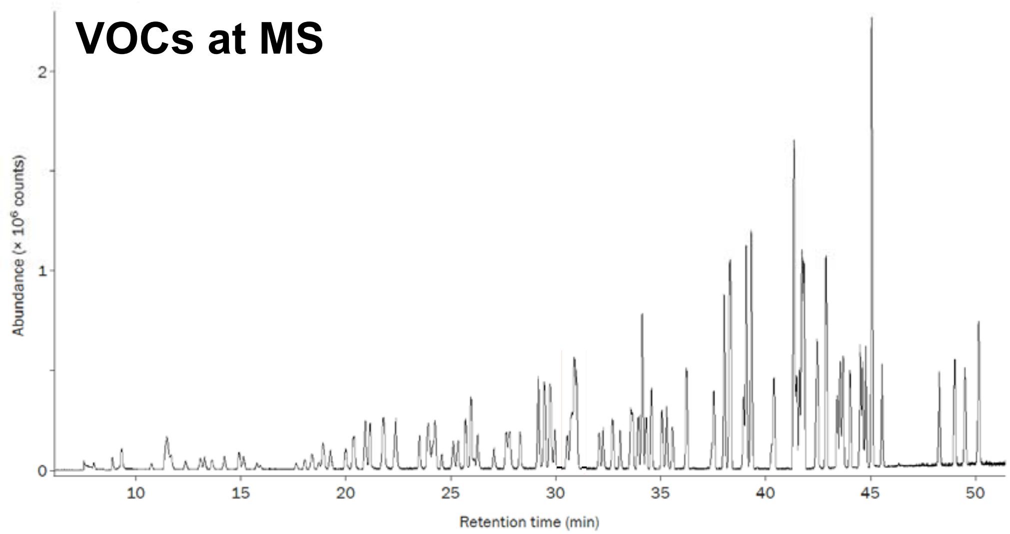
- Formaldehyde must go to the MS
- C_2 and C_3 compounds on FID but also require a stronger column

Results

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



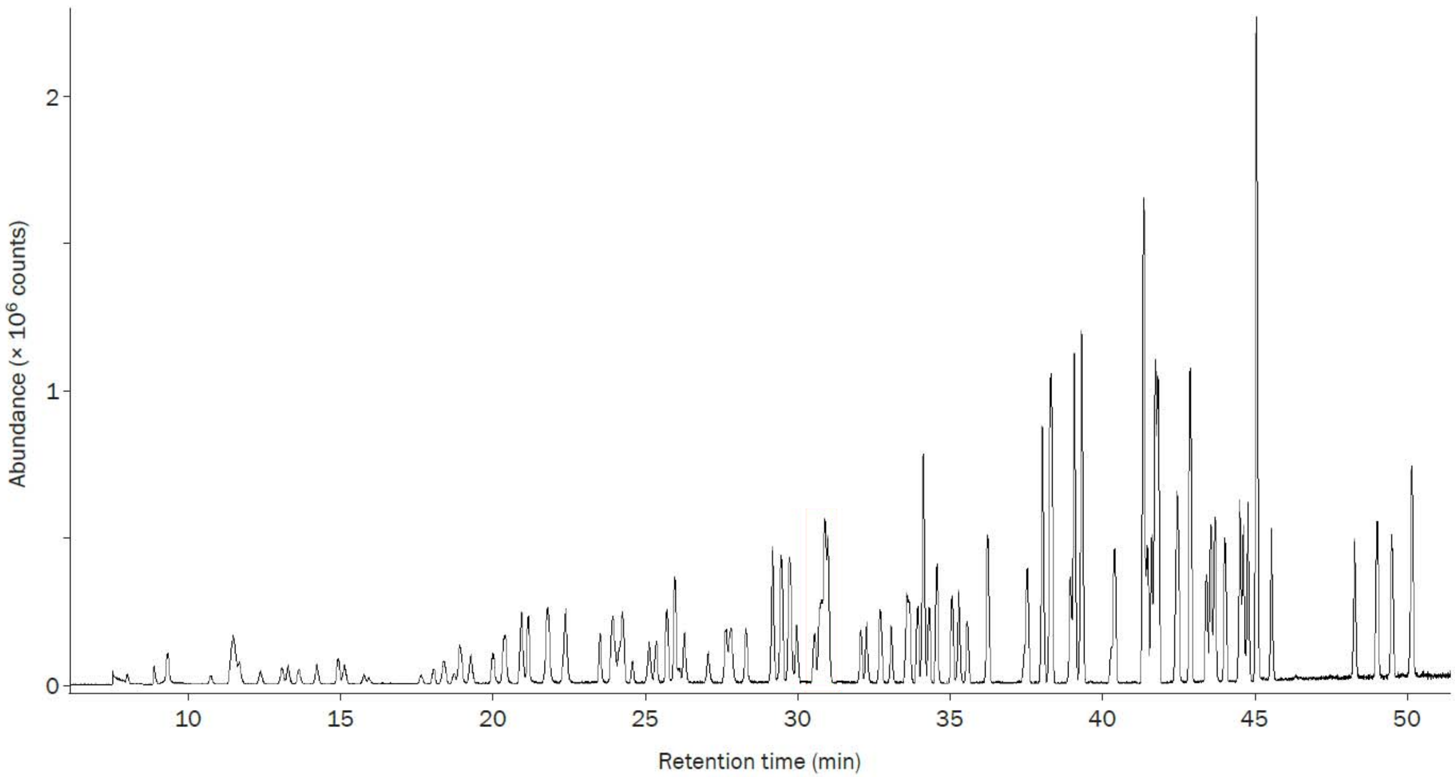
5 compounds



112 compounds

Results

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



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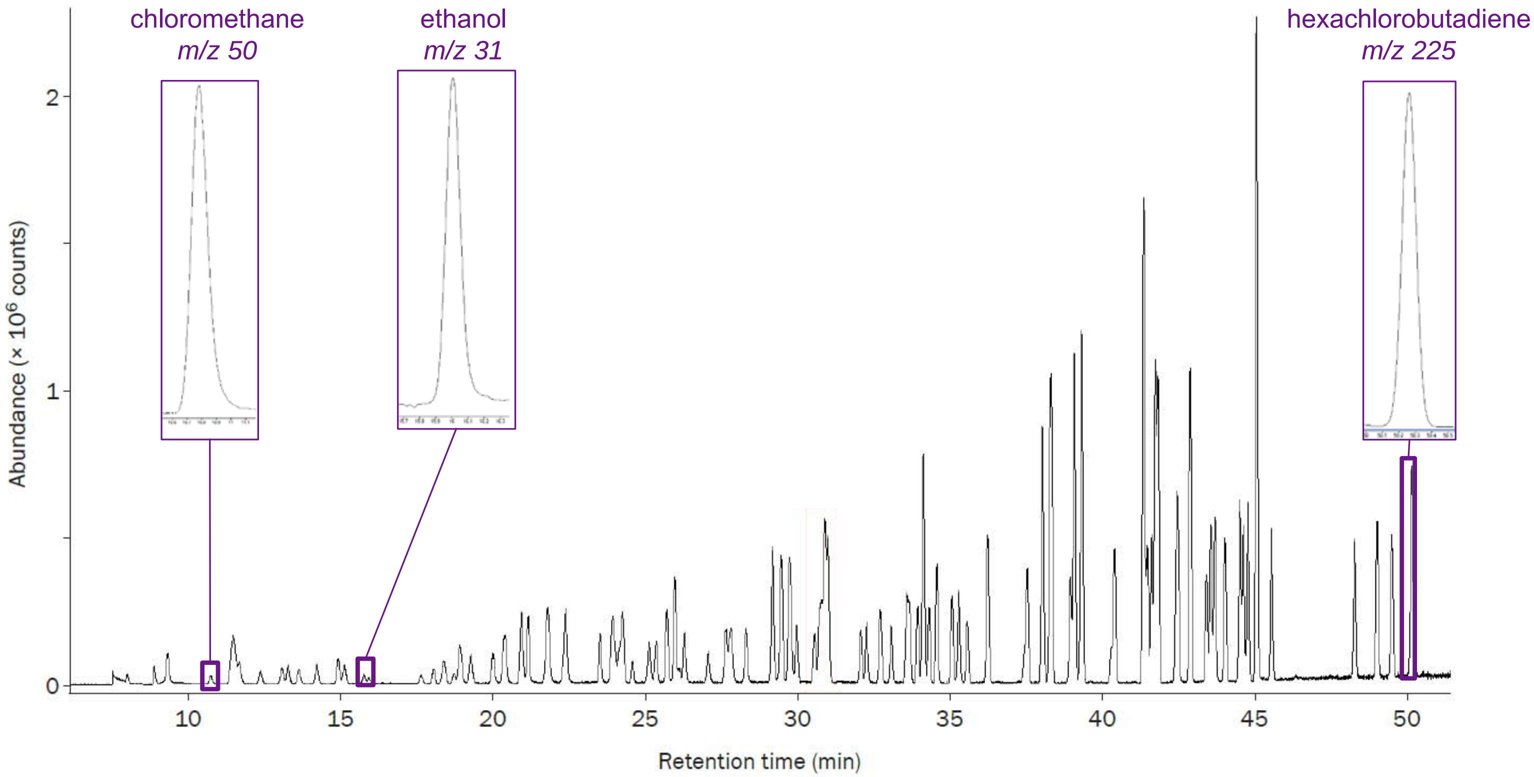

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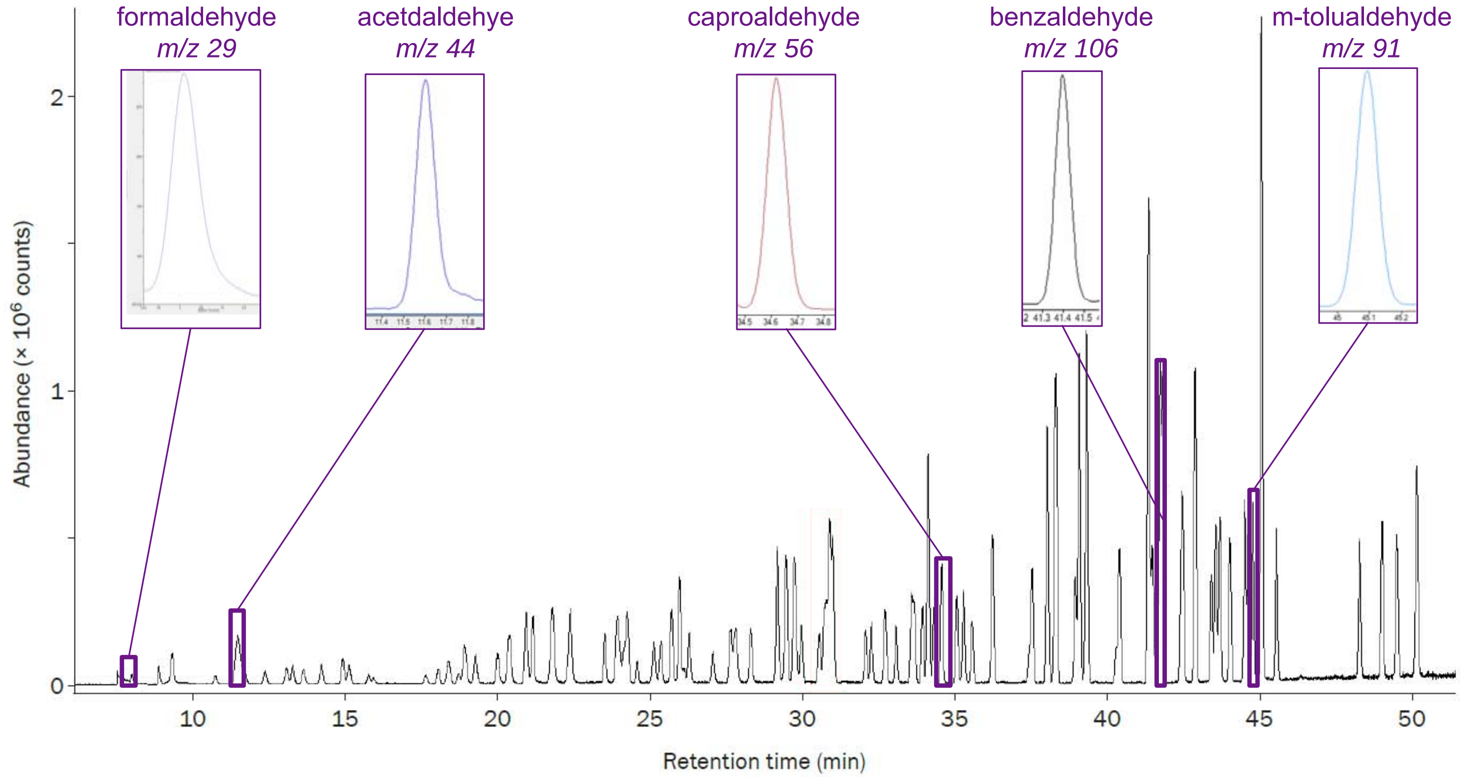

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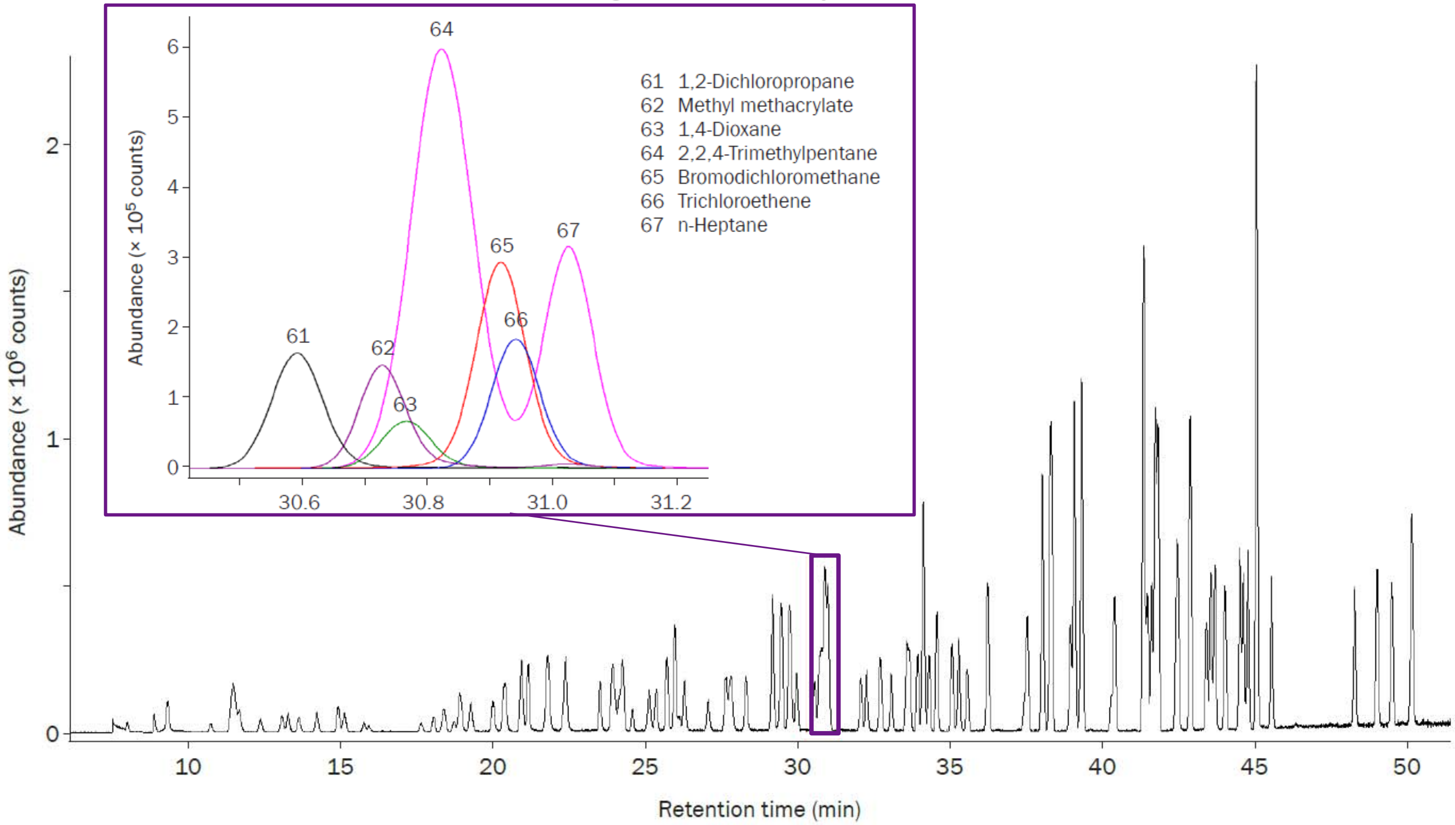
PAMs, TO-15 & OVOC in a single analysis with no liquid cryogen



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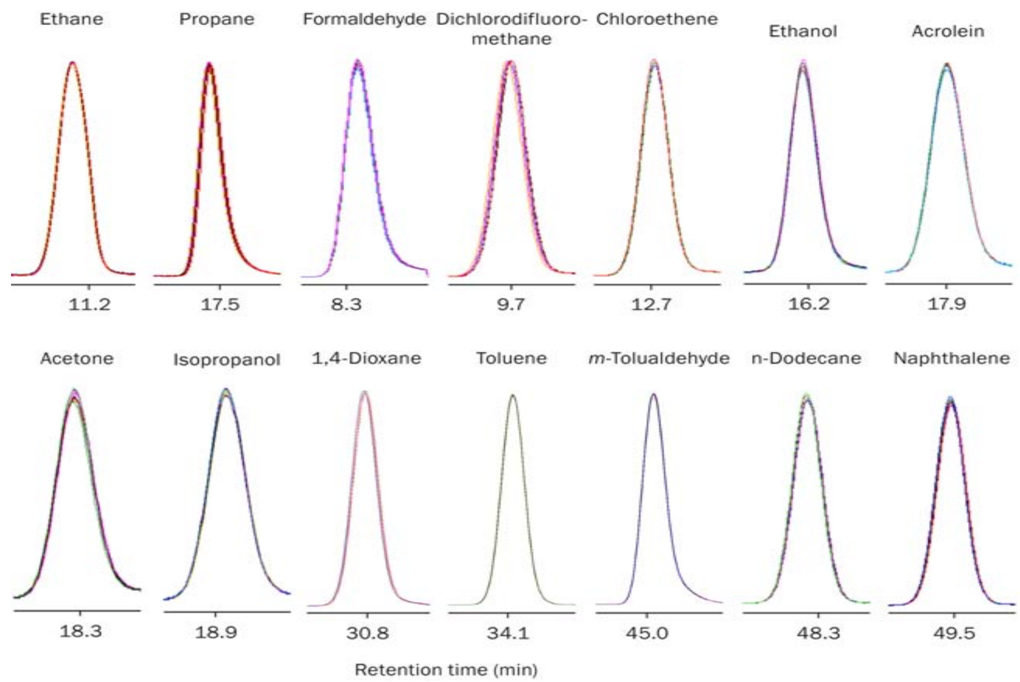
Reproducible unattended analysis

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



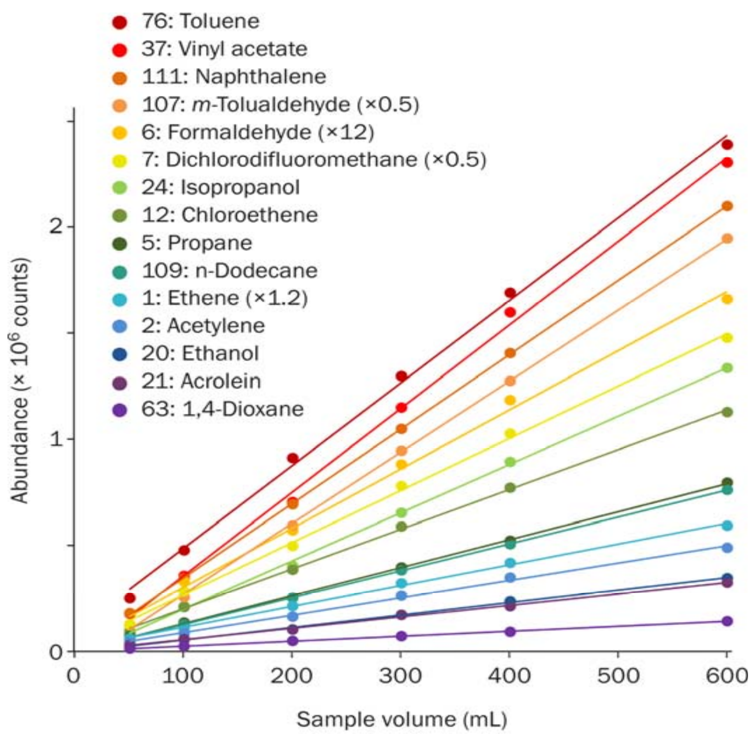
Example compounds covering the polarity and volatility range of the target list: 10 replicate analysis of 10 ppb standard at 100% RH overlay perfectly for all compounds

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-Tolualdehye	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

Beyond TO-15

- Global drive for
  - Broader compound lists
  - Lower detection limits
    - Quantitative retention of very volatile to volatile organic compounds in a single analysis
  - Online, unattended sampling and analysis
  - Faster analysis
    - Trapping and separation of 117 compounds with < 60 minute cycle times
  - Lower cost per sample
  - Flexible sampling options – Canister, Online and tubes
  - Water management with no loss of polar compounds