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international

# Extending the Analysis of Ozone Precursors

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THE QUEEN'S AWARDS FOR ENTERPRISE: INTERNATIONAL TRADE 2015

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# Summary

- What drives innovation?
  - EPA PAMS Update
  - Chinese MoE Environmental Air Volatile Organic Compound Monitoring Program
- Current Technologies
- Advancements in Water Management
- Application and performance data

# EPA PAMS Update

- Published in to Federal register on the 27th October 2015.
  - http://www.gpo.gov/fdsys/pkg/FR-2015-10-26/pdf/2015-26594.pdf

- What the update details
  - Addition of new priority compounds
    - **α/ β pinene**
    - **Ethanol**
    - Carbon tetrachloride

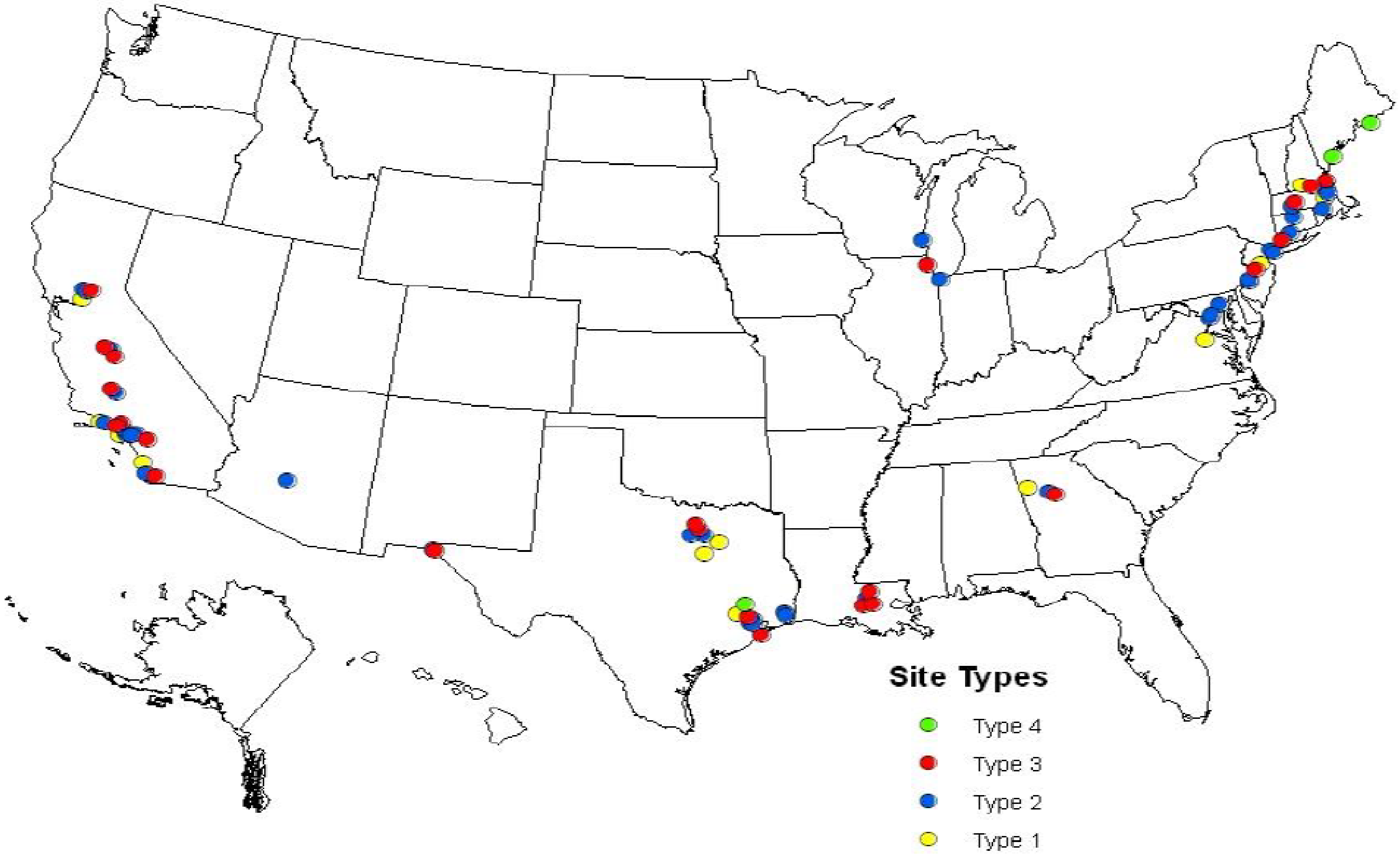
  - Replacement of 20 year-old multi-site, ozone network design with an updated 2-part network design
  - Requires PAMS measurements to be taken at existing NCore sites in areas with population of 1 million or more irrespective of Ozone NAAQS attainment status

**JUNE 2019 monitoring begins!**

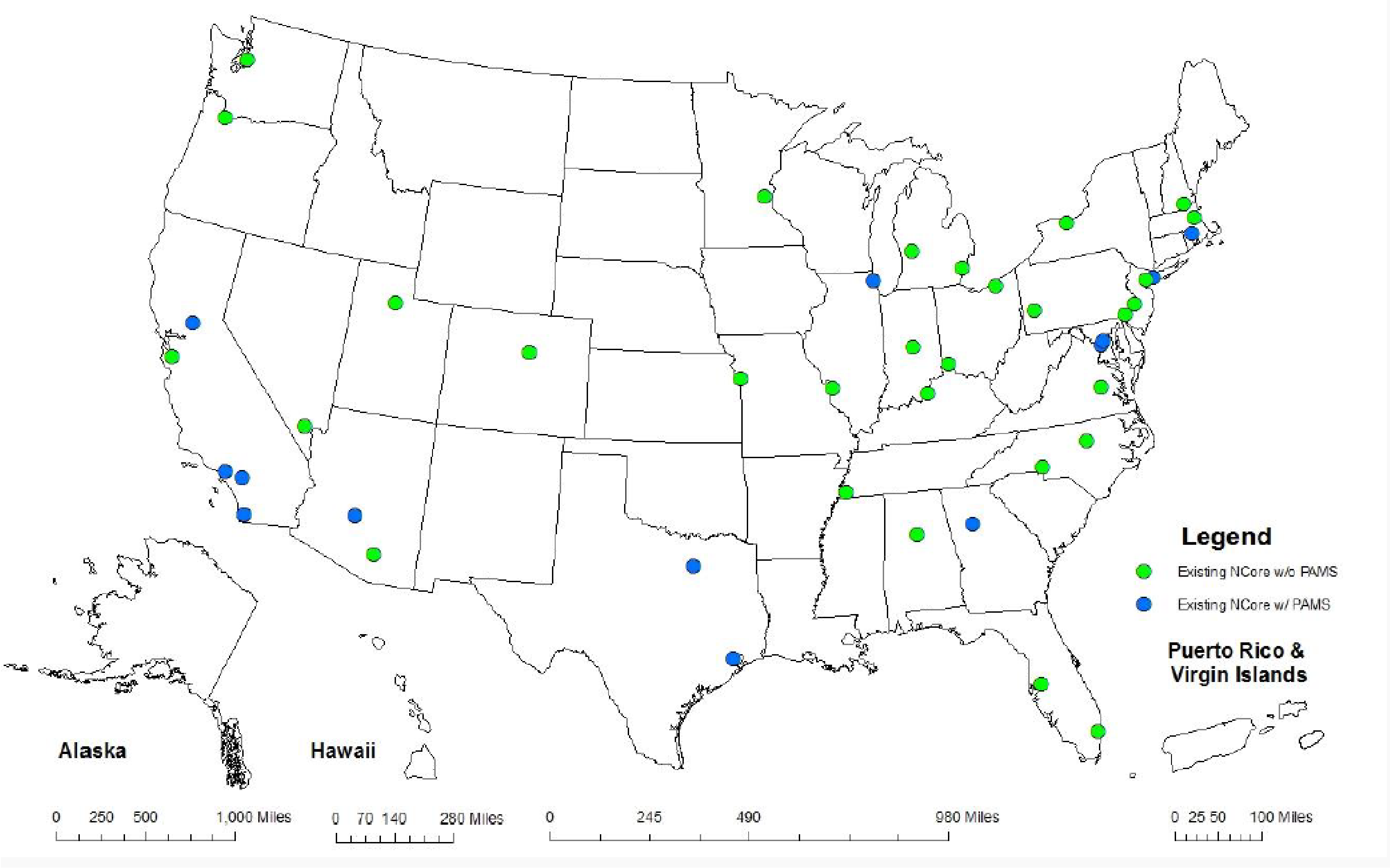
**Early Adopters 2017/2018!**

**Markes finished 1st in both stages of the evaluation**

# Current PAMS Sites



# Proposed PAMs sites



# EPA PAMs Evaluation

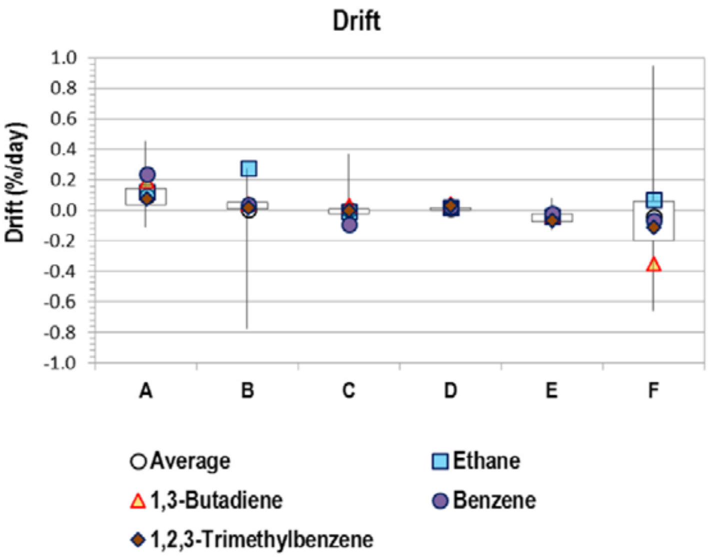
- Laboratory evaluation carried out in Spring 2014, based in RTI laboratories, 8 vendors were tested with controlled gasses to evaluate performance (precision, bias, impact of temperature and humidity) and operation of the autoGC.
  - Final report available at – https://www3.epa.gov/ttnamti1/files/ambient/pams/labevalreport.pdf
    - Agilent-Markes system was vendor 1
    - Thermo-Markes system was vendor 3

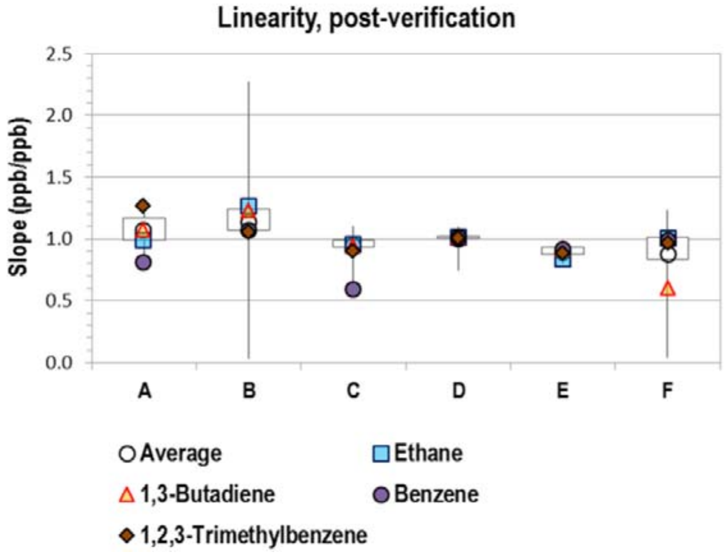
- Field Evaluation was carried out between spring 2015 and spring 2016. System was installed in a mobile trailer to test for field ruggedness and robustness
    - Final report available, **https://www3.epa.gov/ttn/amtic/files/ambient/pams/FINAL-AutoGC-Field-Evaluation-Report.pdf**
      Agilent-Markes system was vendor D
      Thermo-Markes system was vendor E

# Summary of Field Evaluation

Agilent- Markes = D, Thermo-Markes = E

| Test | Vendor | | | | | |
|---|---|---|---|---|---|---|
| | A | B | C | D | E | F |
| Precision (%RSD) | 32.3 | 13.1 | 6.3 | 1.6 | 16.7 | 34.9 |
| Bias (MNB, % unsigned) | 23 | 17 | 8 | 2 | 12 | 27 |
| Drift (%/day) | 0.09 | 0.00 | 0.00 | 0.01 | -0.04 | -0.05 |
| Linearity (slope, ppb/ppb) | 1.07 | 1.14 | 0.95 | 1.01 | 0.90 | 0.88 |
| Completeness (%) | 87.1 | 93.7 | 98.6 | 100.0 | 100.0 | 95.0 |
| MDL (ppb as carbon) | 1.22 | 0.41 | 0.32 | 0.17 | 0.40 | 1.40 |


Drift


Linearity, post-verification

# Chinese MoE

Environmental Air Volatile Organic Compound Monitoring Program

- New document issued in December 2017

- New requirement in the monitoring of both PAMS and TO-15 analytes in a single run for a total **of 108 compounds**.
  - Techniques must not compromise peak shape and chromatographic separation of this combined compound list

- Technique historically required cryogenic cooling of the GC column, but with the associated cost and inconvenience (in addition, many thermal desorption (TD) systems also require cryogen), not feasible for implementation in many areas.

# Instrumentation

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# Method compliant canister analysis …

… with UNITY–CIA *Advantage*-xr

- Standard features of the CIA *Advantage* HL-xr ensure full compliance with US EPA TO-15,US EPA PAMS, Chinese EPA HJ 759 and other standards.

  - Internal standard addition.
  - Ability to analyse samples of high and unknown concentration.
  - Dry-purge of focusing trap.
  - Reverse flow during trap desorption.
  - Electronic mass flow controllers for purge, carrier and sample gases.

# How on-line analysis with the CIA Advantage-xr works

1. Air/gas focusing

Peltier-cooled focusing trap eliminates ice-plug formation, while fast trap cooling minimises cycle times.

Samples are introduced directly onto the electrically-cooled, sorbent-packed focusing trap of the UNITY-xr thermal desorber, typically held between ambient and –30°C.

# How on-line analysis with the CIA Advantage-xr works

2. Trap desorption and outlet split

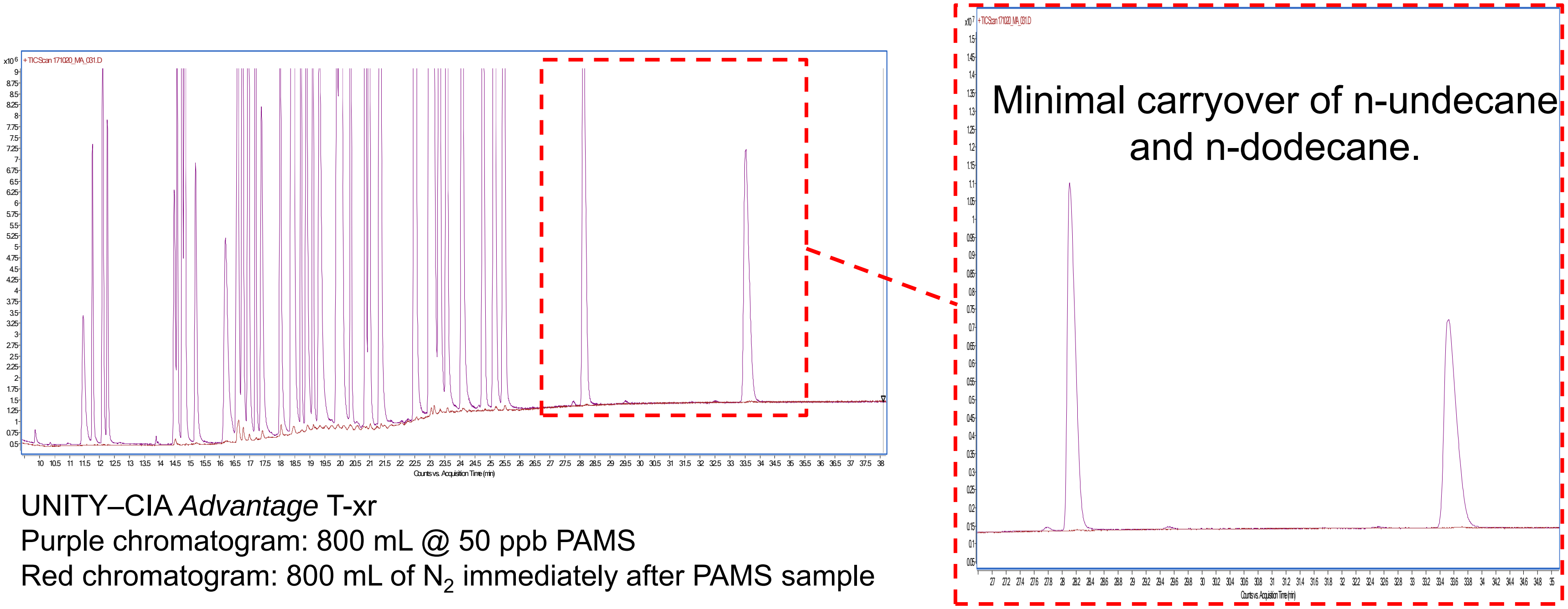
Focusing trap rapidly heated (up to 100°C/s) in a reverse flow of carrier gas (‘backflush’ operation), to transfer the analytes to the GC column.

- Fully automated sequences of air/gas (from a sample stream, calibration gas or zero air/gas) can be set at user-defined frequencies.
- During trap desorption, the flow of analytes can be split and re-collected onto a clean sorbent tube.
- Tubes and traps can contain multiple sorbents, for analysis of an extended range of analytes.

# Concentration versatility

Enhanced purging of sample lines minimizes carryover

- Optional post sampling purge stages, with either carrier or humidified gas, minimize carryover after very high concentration samples.
  - Boosts data confidence and productivity.
  - Flexibility: both high and low concentration samples can be included in a single sequence.



Minimal carryover of n-undecane and n-dodecane.

UNITY–CIA *Advantage* T-xr
Purple chromatogram: 800 mL @ 50 ppb PAMS
Red chromatogram: 800 mL of $N_2$ immediately after PAMS sample

# Water Management

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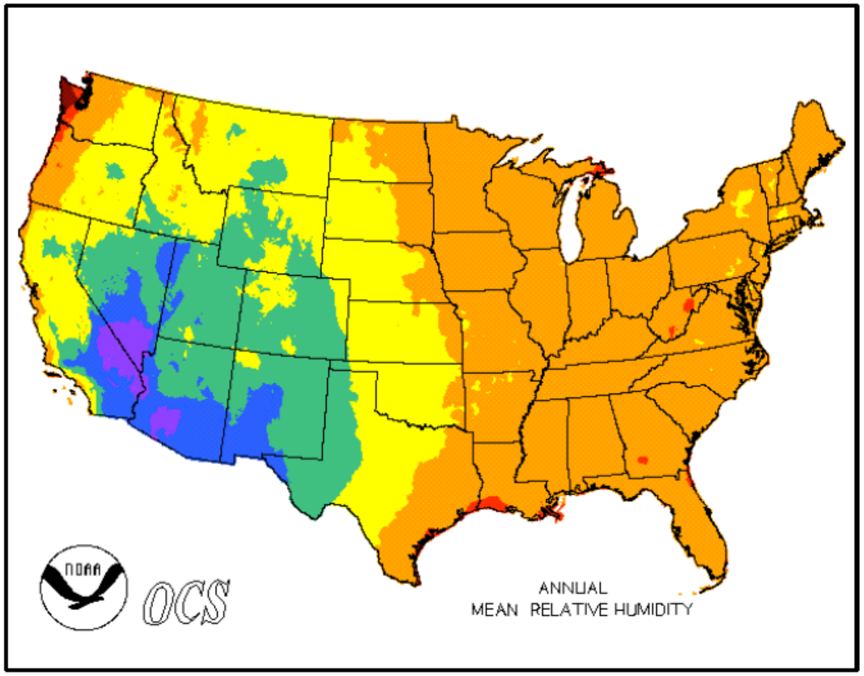
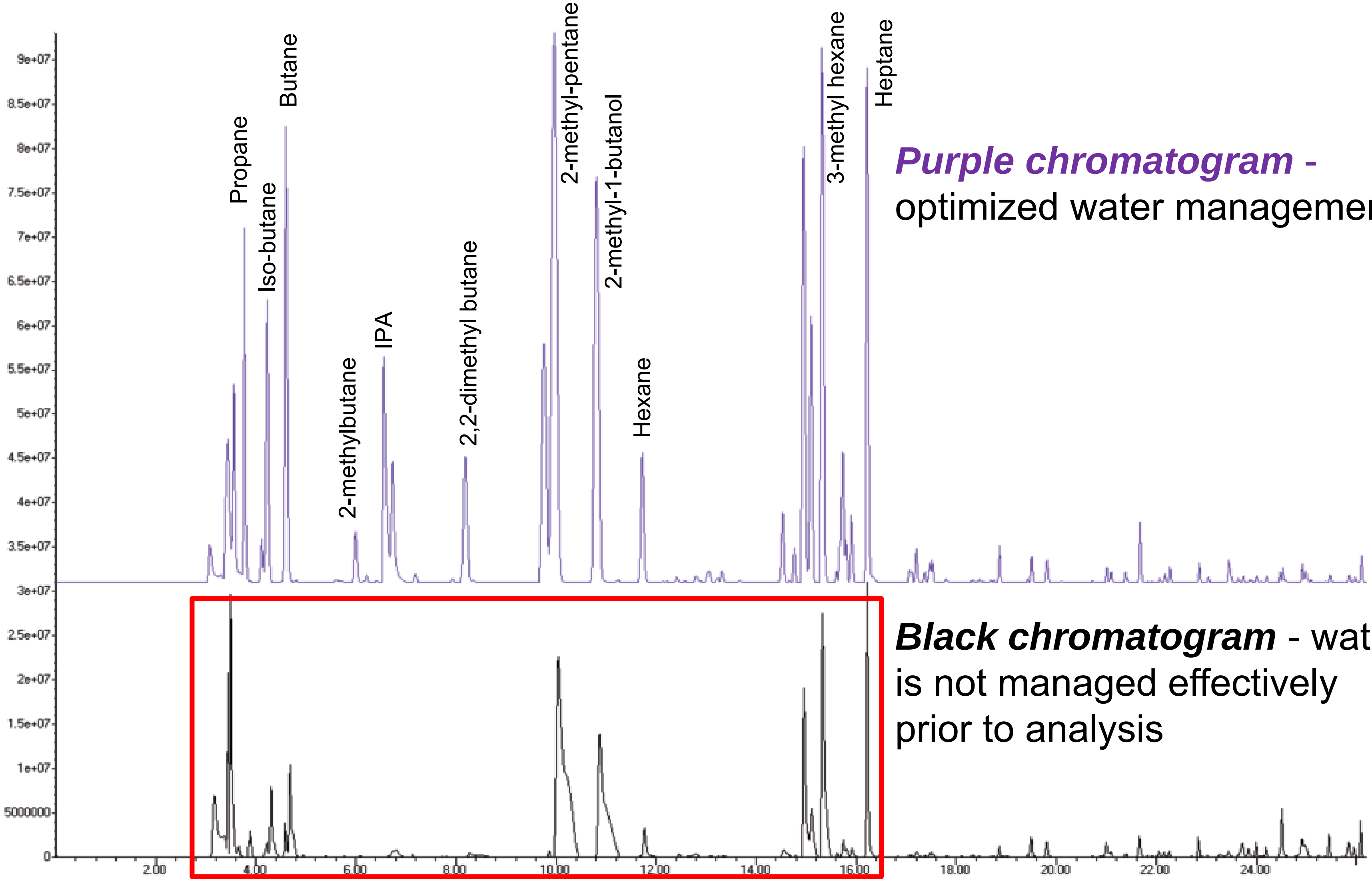
# Ambient Air –
# Average Annual Relative Humidity for the USA

- Variation across the country dependant on a number of factors not limited to but including
  - Local weather events
  - Altitude
  - Environment
  - Local industry
  - Etc.
- Analytical systems for air analysis must be equipped with a number of options to handle water
- High levels of water introduced into the system can cause problems with recovery and analysis of compounds of interest and in extreme cases can cause issues with detector response.



🟪 C 26 - 35
🟦 D 36 - 45
🟩 E 46 - 55
🟨 F 56 - 65
🟧 G 66 - 75
🟥 H 76 - 80
🟫 I > 80

# No water management of humid samples



***Purple chromatogram* -** optimized water management

***Black chromatogram*** - water is not managed effectively prior to analysis

***Lower* response and *poor peak* shape observed when water is not eliminated**

# On- Line/Canister Analysis water management

Previous Solutions - Ambient temperature trapping and dry purging

- Selection of appropriate sorbent materials and trap temperature eliminates most of the water.

| Sorbent Type | Volatility range |
|---|---|
| Porous Polymer | $C_6$-$C_{30}$ |
| Graphitized Carbon Black | $C_{4/5}$-$C_{14}$ |
| Carbon Molecular Sieve type | $C_2$-$C_5$ |

Increasing water retention

- Typical applications
  - VOCs (US EPA Methods TO-15 and NJ LL TO-15).
  - Stack emissions (CEN/TS 13649 or Chinese EPA Method HJ 734)

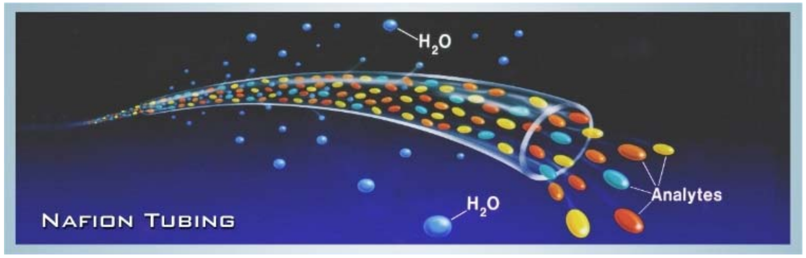
- Advantage
  - Large volume trapping with minimal water retention

- Disadvantage
  - Very volatile species cannot be trapped under these conditions.

# On- Line/Canister Analysis water management

Previous Solutions

Nafion Dryer



- Hydrophilic co-polymer widely used for the analysis of $C_2$–$C_{10}$ ozone precursors.
- Applications
  - Ozone precursors (PAMS Method).
  - VOCs and VVOCs (Chinese EPA Method HJ 759).
  - Hazardous air pollutants.

- Advantage
  - Ideal for GC–FID analysis of VOCs as it removes possible interferents resulting in ‘cleaner’ chromatography.

- Disadvantages
  - Removes polar and other compounds that could be of interest.
  - High gas consumption required to dry the sample gas

# Analysis of VVOC and Polar VOCs

- Historical options

| | Polar compounds | VVOCs |
|---|---|---|
| **Nafion dryer** | X | ✓ |
| **Ambient temperature trap** | ✓ | X |

**2 RUNS REQUIRED**

- NOW available with Kori-xr

| | | |
|---|---|---|
| **Kori-xr** | ✓ | ✓ |

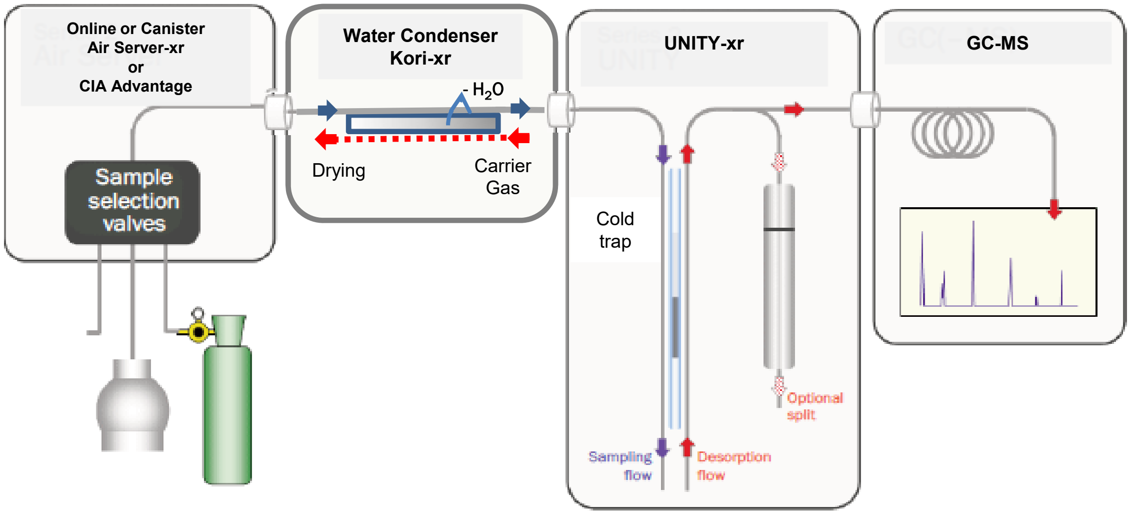
**All IN 1 RUN!**

# Introducing Kori-xr

## Water abstraction device

- Below -30°C water deposition (phase transition from gas to solid) will occur.
- Water trap placed before sorbent trap enables water to be removed from sample.
- Loss of polar compounds minimised.

氷



*Kori-xr was developed in collaboration with the University of York (in UK) under a Knowledge Transfer Program.*

# Kori-xr
# Innovative on-line water management solution

## 1. Air sampling and water removal

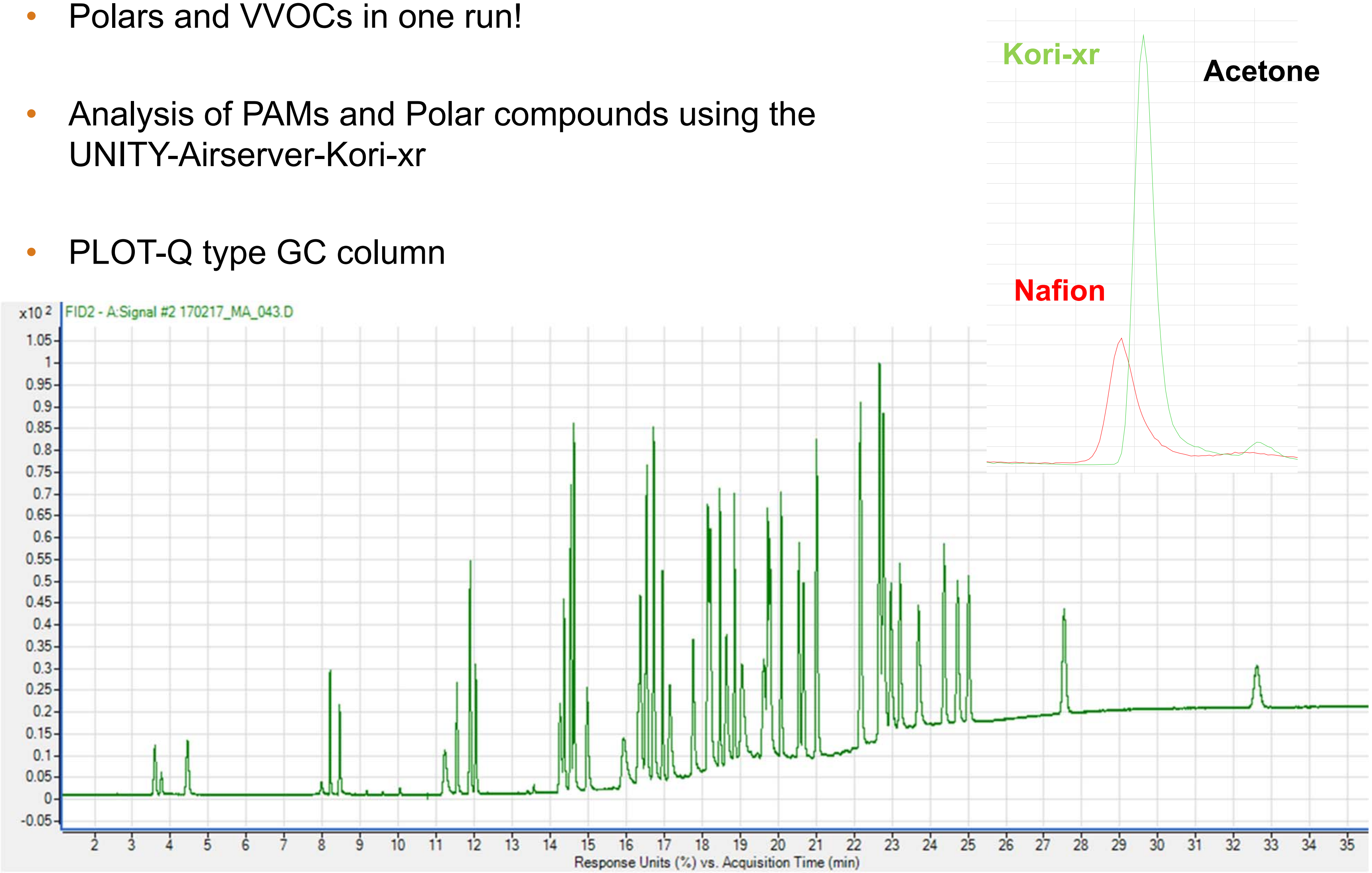
The empty Kori-xr trap, held at –30°C, sits in-between the sample inlet and the focusing trap, causing only vapour-phase water to be deposited directly in it as ice, before it reaches the trap. VOC not affected.

## 2. Trap desorption and water purging

While the sample is being transferred to the GC, the Kori-xr trap is heated in a reverse flow of gas, causing the trapped water to be expelled and preparing Kori-xr for the next sample.

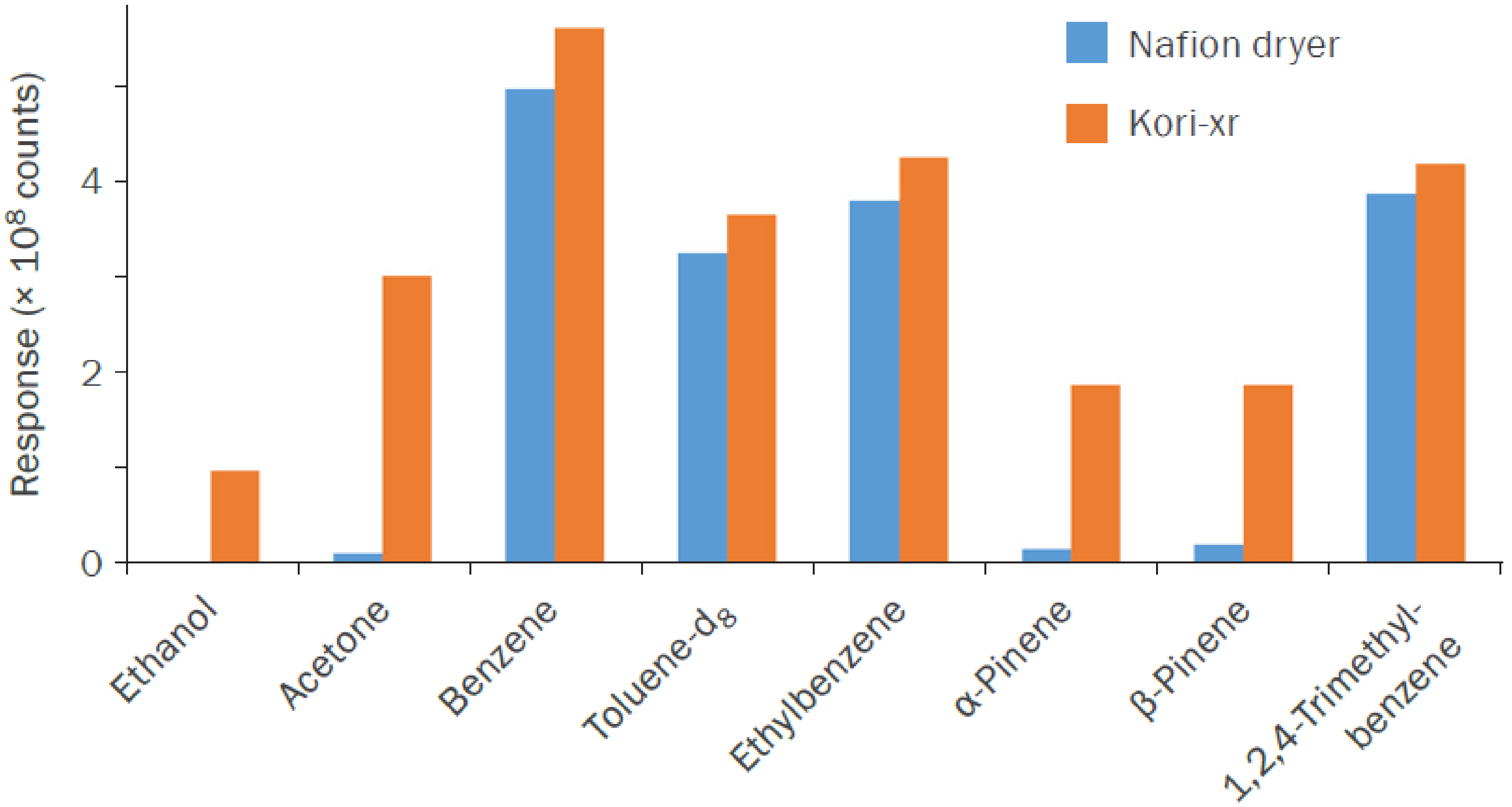
# “New” PAMS chromatogram

- Polars and VVOCs in one run!
- Analysis of PAMs and Polar compounds using the UNITY-Airserver-Kori-xr
- PLOT-Q type GC column



## Kori-xr *vs.* Nafion Dryer

### Improved retention of ultra-volatile and polar species



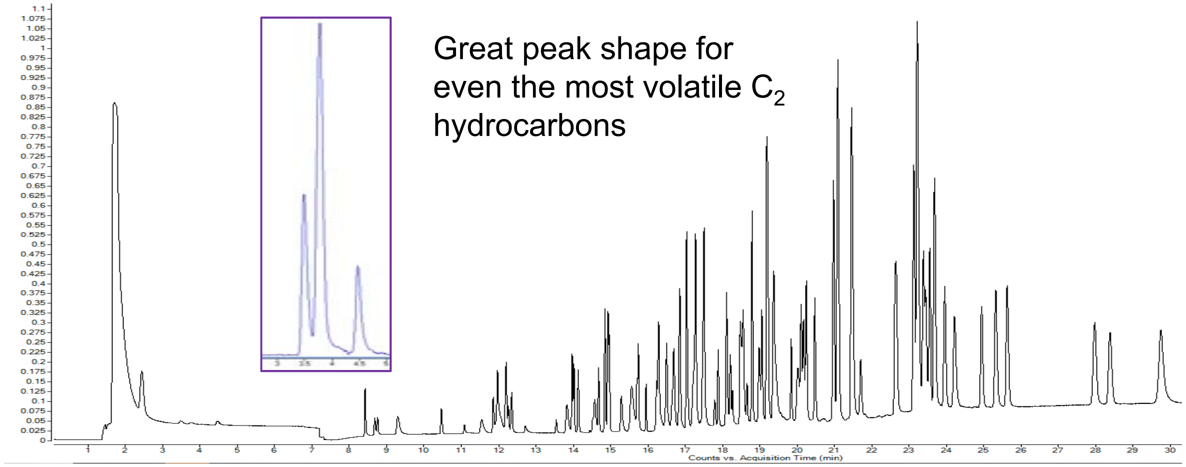
Comparison of Kori-xr v. Nafion Dryer at 80% relative humidity

# Dry-Focus3

The unique triple-step focusing and water management mechanism that operates cryogen-free.

- Dry-Focus3 leverages the power of Kori-xr and the splitless performance of UNITY-xr to deliver 0.01 ppb (10 ppt) detection limits or better for air toxics using regular GC-QMS.

- Dry-Focus3 is **compatible with polar and apolar compounds, terpenes, and $C_2$ hydrocarbons**.



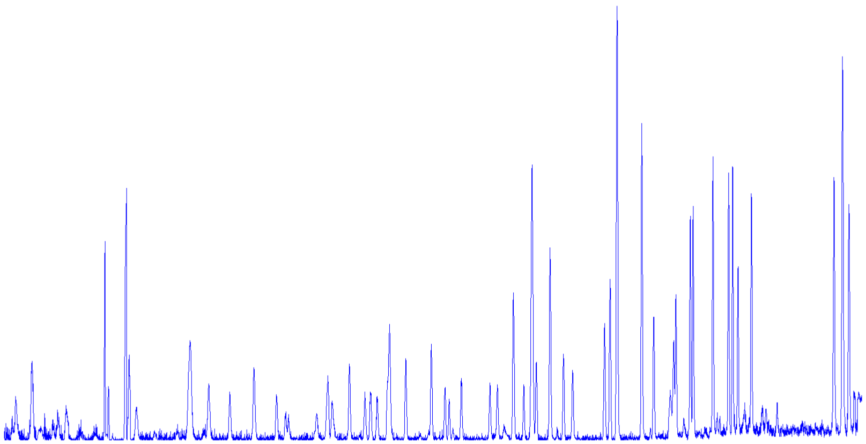
Great peak shape for even the most volatile $C_2$ hydrocarbons

# Exceeding TO-15 requirements

The ultimate analytical performance for an expanded range of air toxics with optimum sensitivity and cryogen-free operation.

- Excellent linearity, reproducibility, retention time stability and detection limits for even the most challenging compounds at trace levels.

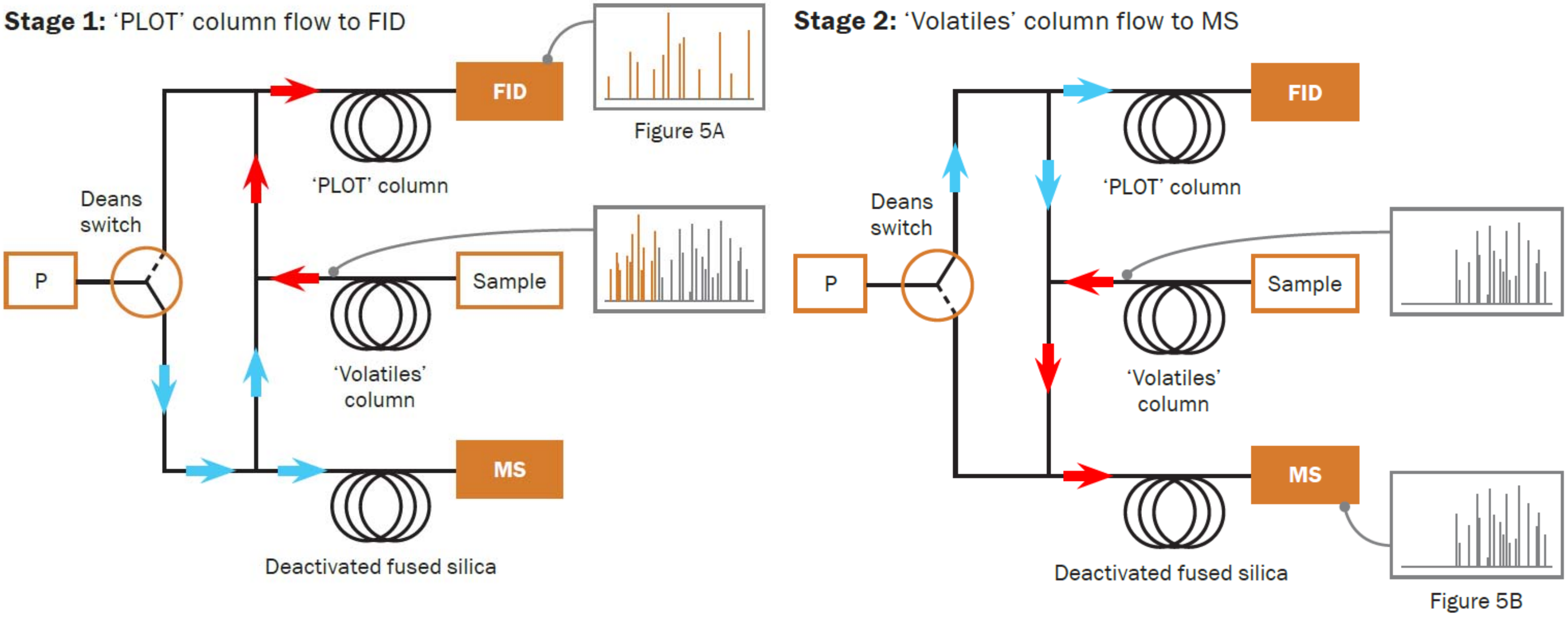
| | RSQ (50-1000 mL) | RSD RRF (%) | RT RSD (%) | MDL (ppbv) |
|---|---|---|---|---|
| Chloromethane | 0.999 | 15.3 | 0.10 | 0.02 |
| Bromomethane | 0.995 | 2.4 | 0.04 | 0.05 |
| Acrolein | 1.000 | 3.2 | 0.05 | 0.02 |
| Acetone | 1.000 | 2.1 | 0.03 | 0.03 |
| Isopropyl alcohol | 0.982 | 27.1 | 0.03 | 0.06 |
| Tert-Butyl Methyl Ether | 0.999 | 4.0 | 0.04 | 0.01 |
| Vinyl acetate | 0.998 | 4.7 | 0.03 | 0.01 |
| Methyl ethyl ketone | 0.995 | 7.8 | 0.02 | 0.01 |
| Ethyl acetate | 0.999 | 7.9 | 0.01 | 0.01 |
| Tetrahydrofuran | 0.998 | 2.3 | 0.02 | 0.01 |
| Methyl methacrylate | 0.999 | 6.9 | 0.01 | 0.01 |
| p-Dioxane | 0.989 | 19.0 | 0.01 | 0.04 |
| 2-Pentanone, 4-methyl | 0.999 | 8.8 | 0.01 | 0.006 |
| Methyl n-butyl ketone | 0.998 | 1.9 | 0.01 | 0.009 |



1 L, 100 % RH, 0.05 ppbv TO-15 standard
UNITY–CIA *Advantage*–Kori-xr

# Removing the need for cryogenic GC oven cooling

Deans Switch Set up



→ = Analyte flow

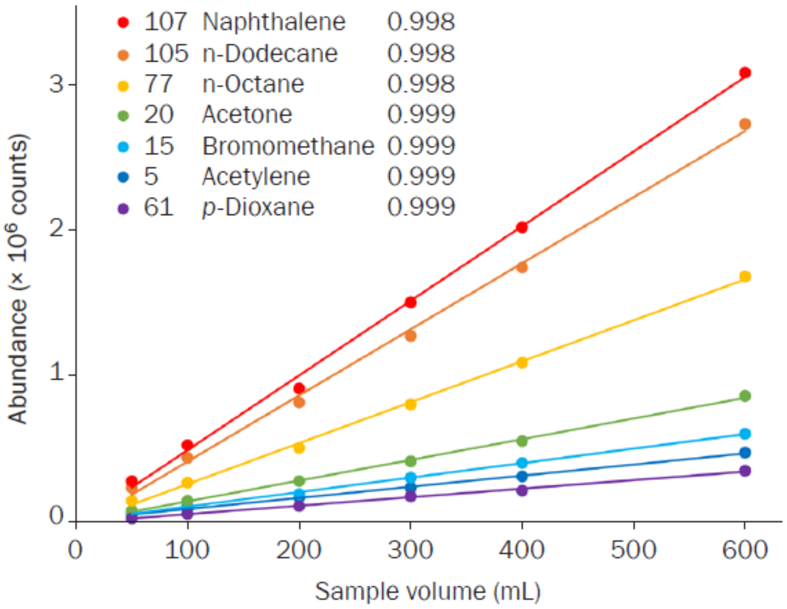
→ = Gas flow

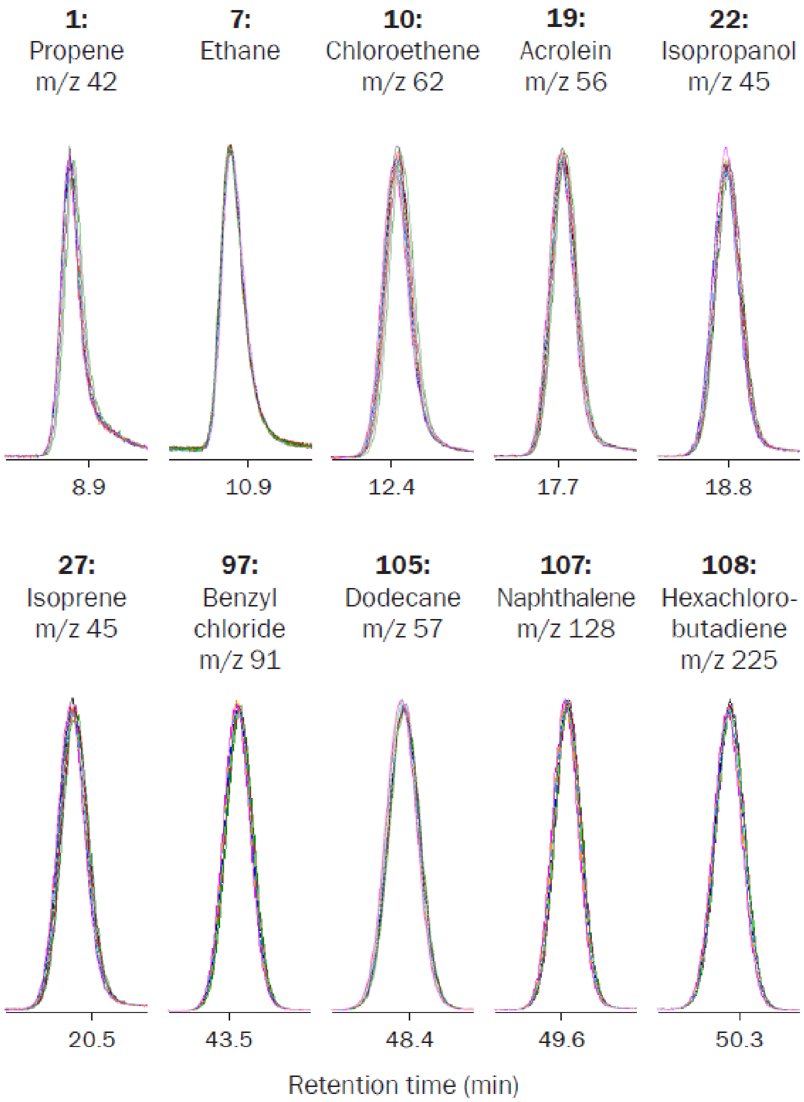
P = Carrier gas pressure supply

For the first ~8 minutes of the GC run, the Deans switch is set to send the primary column effluent to the secondary column and the FID detector. Once the very volatile C2 hydrocarbons have eluted, the Deans switch switches to 'cut' the primary column effluent to the MS.

# Linearity/Reproducibility of dual technique

- Ten repeat analyses of 400 mL of the 10 ppb, **100% RH** standard, demonstrating excellent retention time and response stability.

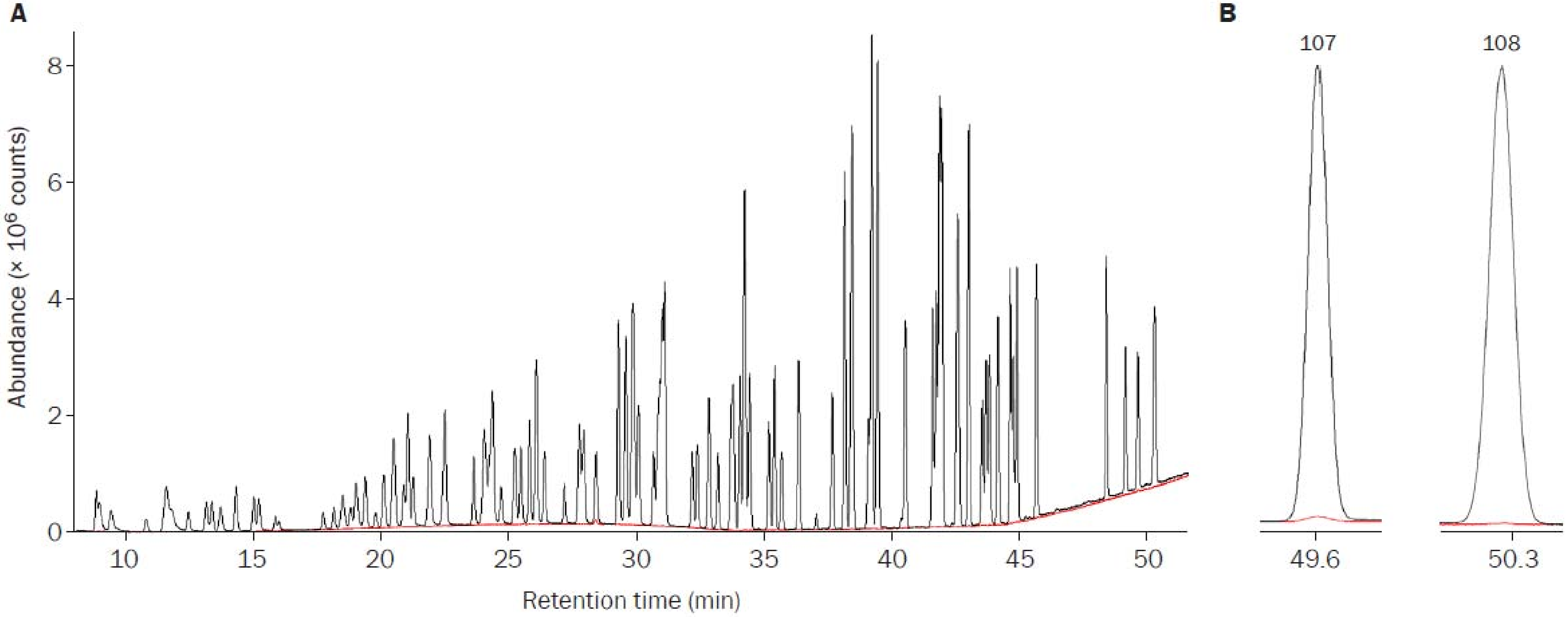




# Stressing the solution

Test of high concentration followed by low concentration

- (A) TIC of 400 mL of the 20 ppb, 100% RH standard (black trace) overlaid with a 400 mL nitrogen blank carryover test (red trace) analysed immediately afterwards. (B) EICs of naphthalene (#107, m/z 128) and hexachlorobutadiene (#108, m/z 225), showing minimal carryover for the least volatile compounds in the list.



# Summary

Take home messages

- Proven Cryogen-free analysis of the **108 ozone precursor and air toxics** compounds listed in the Chinese Environmental Air Volatile Organic Compound Monitoring Program (EA-VOC-MP).
- The **dual-column/Deans switch** GC–MS/FID strategy employed here provides confident identification and quantitation, with **maximum sensitivity achieved** in this challenging application by using the optimum detector for the various compound types.
- Markes' ground-breaking **cryogen-free** Dry Focus3 water management technology has been demonstrated to produce data that satisfies the performance criteria for HJ 759 and EA-VOC-MP, for very volatile C2 hydrocarbons, oxygenated polar VOCs such as acrolein and ethanol, and the less volatile air toxics such as naphthalene, even at **100% relative humidity**.
- The analytical system provides fully automated analysis for **up to 27 sample channels** and offers excellent method detection limits, retention time stability, reproducibility and linearity.
- When combined with the optimised chromatographic method and the **overlap mode** (in which the next sample is loaded to the focusing trap while the current GC analysis is still running), sample-to-sample cycle times of less than 60 minutes can be achieved, **maximising laboratory productivity.**

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