

# Take a deep breath

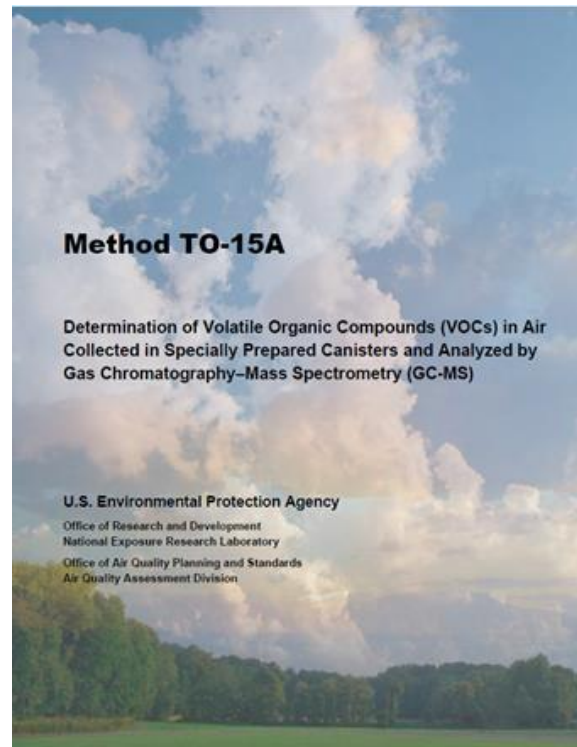
Innovative, cryogen-free, ambient air  
monitoring in compliance with US EPA  
Method TO-15a



# EPA TO-15a

Updates for a thorough and robust method

- Samples and Standards
  - Canister cleanliness criteria
  - Canister qualification
  - Humidity guidance
  - HCF air usage
- Instrumentation
  - Instrument qualification
  - Calibration standard range and regression modeling
  - Quality control criteria
  - Qualitative identification criteria
  - Method detection limits (MDLs)



# Markes TO-15a solution

## UNITY-CIA Advantage-xr with Kori-xr

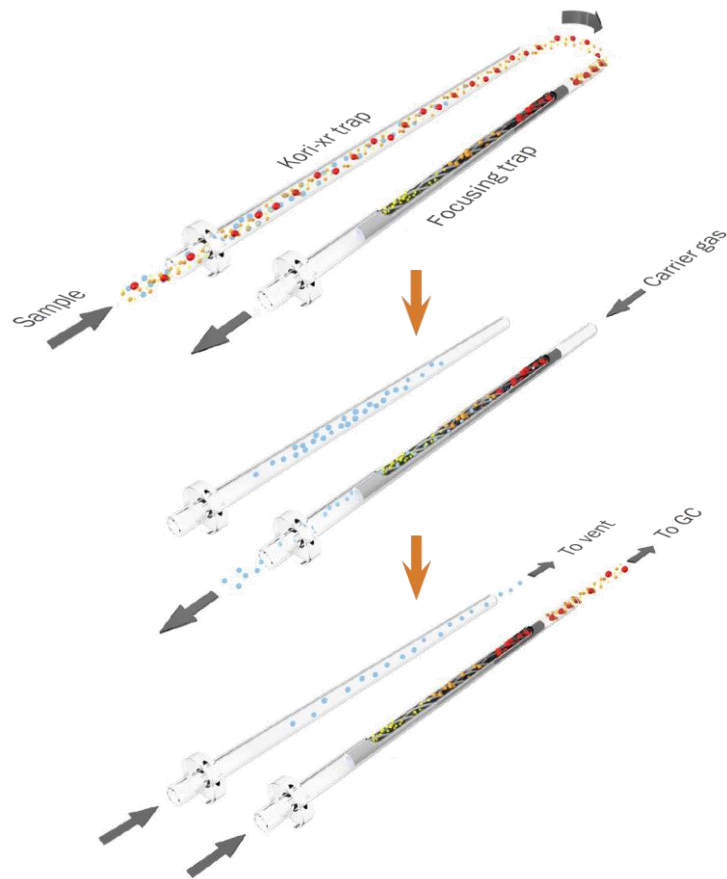
- Unity-xr Thermal Desorber
  - Pre-concentration on TO-15a optimized trap
  - Cryogen-free
- CIA *Advantage*-xr Auto Sampler
  - Vacuum assisted for ambient samples and sample purging
  - Optional humidified purge for post sampling clean-up
- Kori-xr Water Management
  - Efficient removal of water prior to focusing trap



# Markes TO-15a solution

## Water Management with Dry Focus 3

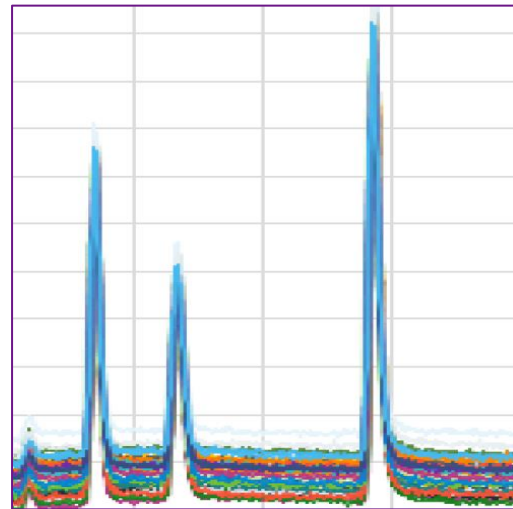
- Three fully-automated stages of operation deliver optimum drying efficiency, sensitivity and selectivity:
  1. Sampling - Kori-xr removes sample humidity while collecting target compounds on electrically cooled focusing trap.
  2. Trap purge – Unity-xr dry purges the focusing trap to remove any residual water.
  3. Desorption - Focusing trap rapidly heats in reverse flow to inject analytes into GC column.



# Markes TO-15a solution

## Water Management with Dry Focus 3

- Lower detection limits
  - Sharper peaks
  - Larger sample volumes can be taken without concern for water interference
- Confidence in results
  - Stabilised retention times
  - Reduced water interference
  - Efficient water removal without loss of polar or oxygenated compounds
- Less instrument downtime
  - Column lifetimes extended
  - More time between cleaning MS



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

# Clean consumables

## Considerations for canisters, water, and gases

- Stainless Steel Canisters
  - Silicon-ceramic lined (SilcoCan®)
  - Extended cleaning using humid and dry gas
- Water for Humidification
  - VOC free needed (LC-MS-grade used)
  - Susceptible to environmental background
- Gases for cleaning and filling
  - Ultra Zero air or 6.0 grade N<sub>2</sub>
  - High purity regulator
  - Moisture and hydrocarbon filter



# Compound Background

Contributions from canisters, water, and air

- Elevated background was battled from a few sources:

- Canisters (C)
- Humidification water (W)
- Environmental air (E)
- Air cylinders (G)

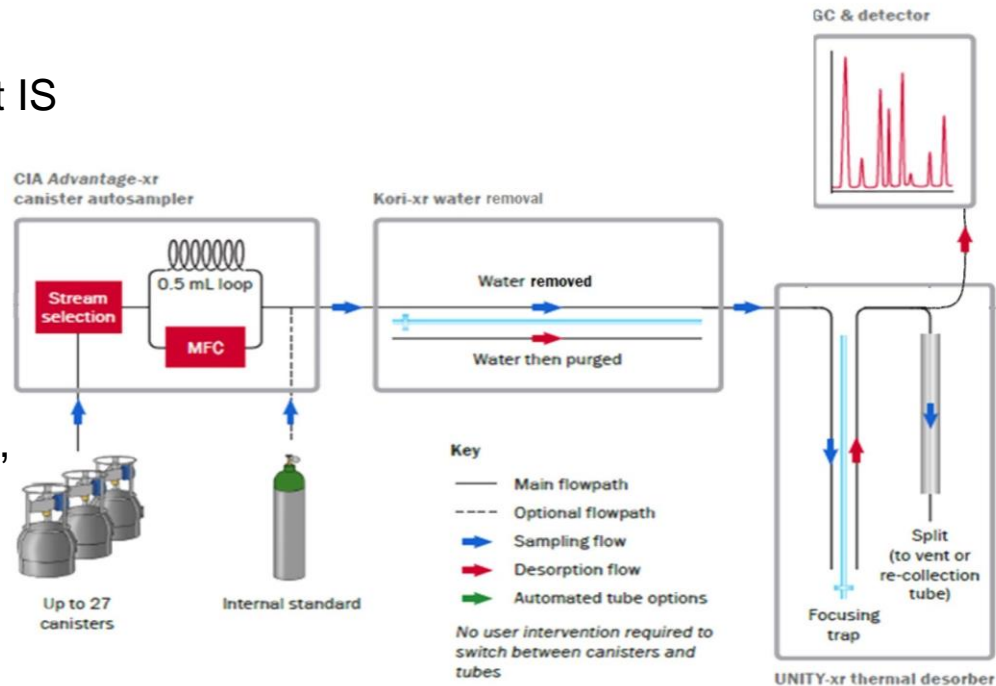


- MDL and ASB blanks
  - Ethanol (C, W, E, G)
  - Acrolein (C)
  - Acetone (C, W, E, G)
  - Isopropyl alcohol (C, W, E, G)
  - 2-butanone (C, E)
  - Tert-butanol (C, E)
- MDL spikes
  - Ethanol (C, W, E)
  - Acrolein (C)
  - Acetone (C, W, E)
  - Isopropyl alcohol (C, W, E)

# Analytical method

## Set up for success

- UNITY-CIA *Advantage*-Kori-xr
  - MFC addition of 4 component IS
  - MFC sampling by volume
  - Water removal at  $-30^{\circ}\text{C}$  during sampling
  - Trap low is  $-30^{\circ}\text{C}$
- GC
  - Rxi-624Sil MS, 60m x 320 $\mu\text{m}$ , 1.8 $\mu\text{m}$  film
  - 20.5 minute run time
- MS
  - Single quad using SIM/Scan

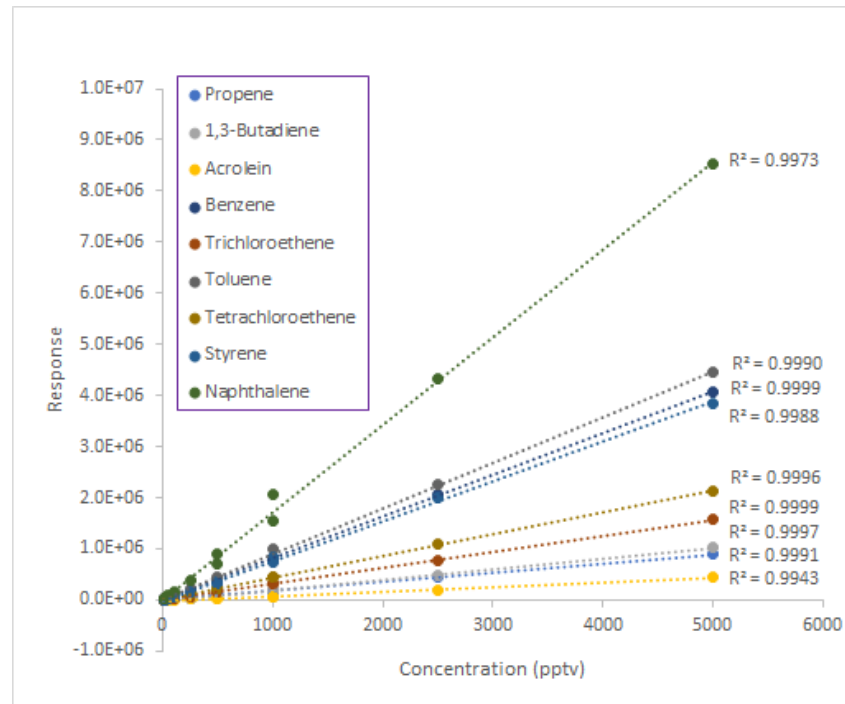




# Initial Calibration

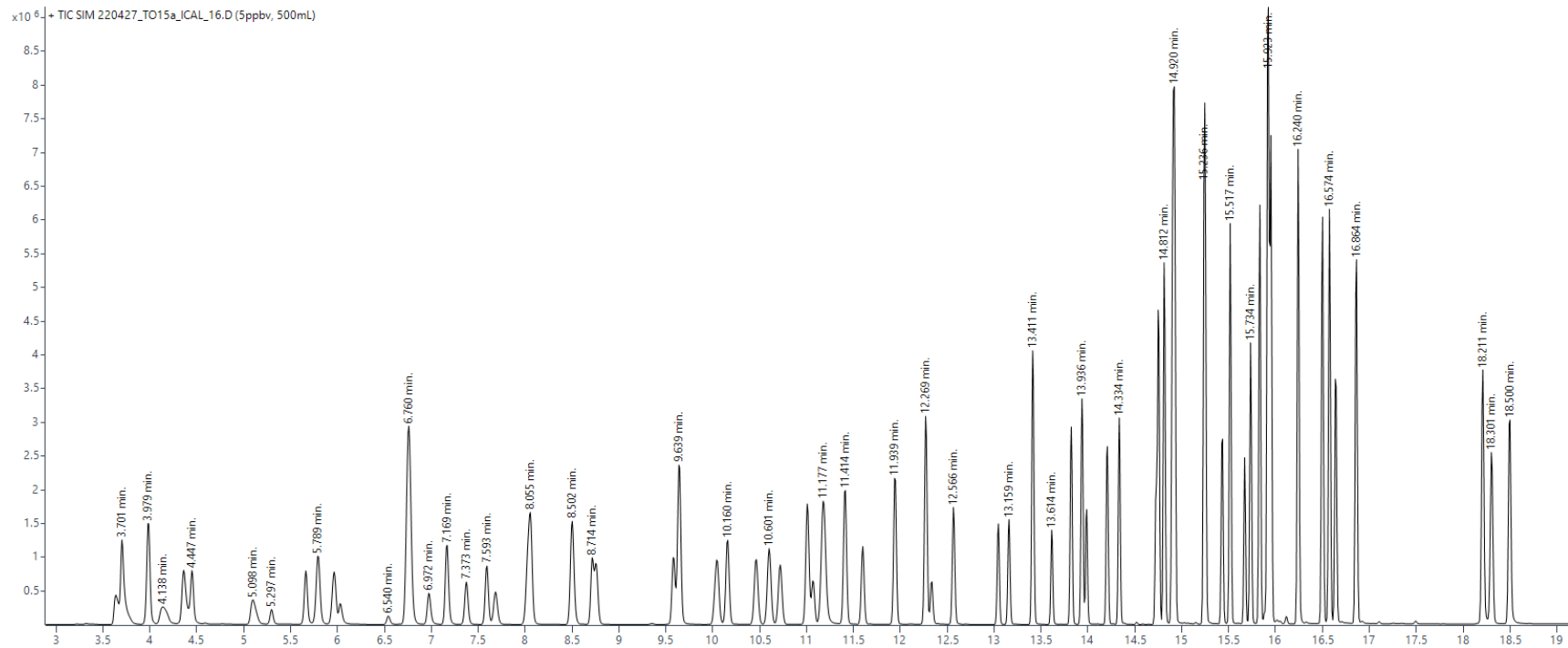
## Calibration at extremes of method requirements

- Standards prepared with Ultra Zero Air at 50% RH
- Two canisters used
  - 1 ppbv and 5 ppbv concentrations
  - Volumes ranged from 5-500 mL by MFC loading
- Average RF RSD values  $\leq 30\%$  for all 75 compounds.
  - Calibration range began at 10 pptv for all compounds



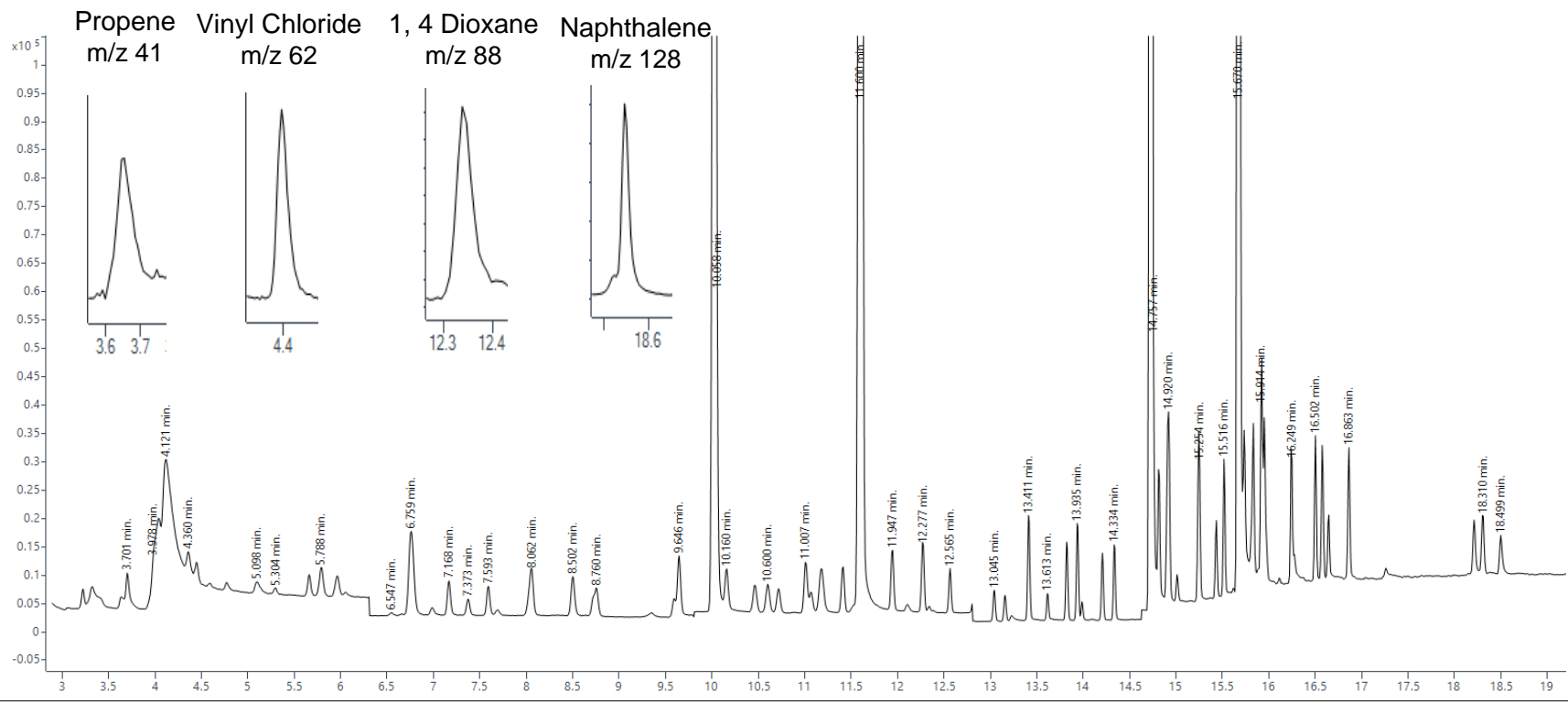
# Example chromatogram

TIC SIM of 75 Component Toxic Organics at 5000 pptv



# Example chromatogram

TIC SIM of 75 Component Toxic Organics at 20 pptv



# Method detection limit blank

Proven cleanliness for real-world use

- Blank canisters were prepared at 50% RH with Ultra Zero air.
- Sampled volume was 500mL.
- 69 of 75 compounds had MDL blank values <20 pptv
  - 67 compounds were <10 pptv
  - 61 compounds were <5 pptv
  - **24 compounds were not detected**

Compound	MDL Blank
Propene	14.41
1,3-Butadiene	0.00
Benzene	6.10
Trichloroethene	0.00
Toluene	5.95
Tetrachloroethene	0.33
Styrene	1.99
Naphthalene	4.96

# Method detection limit spike

Proven accuracy for real-world use

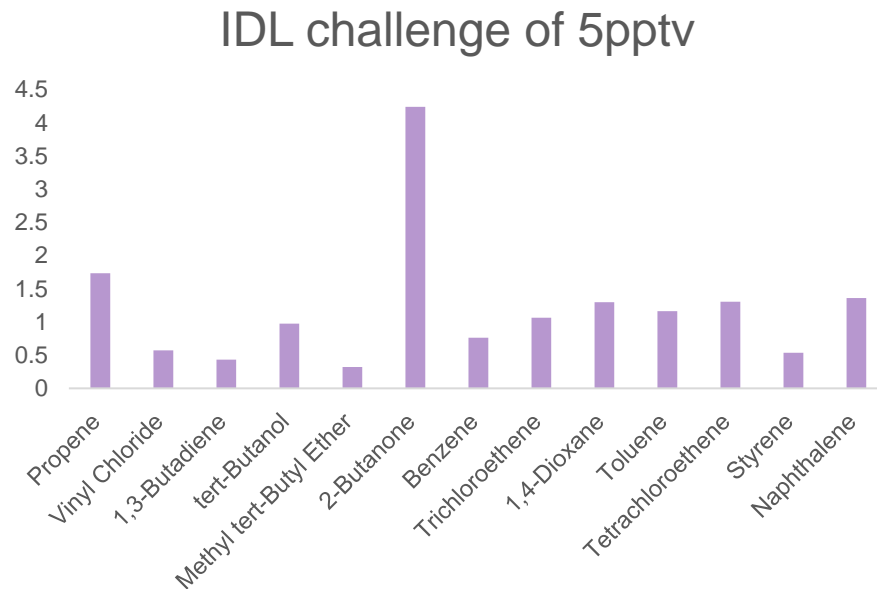
- 10 pptv spiked canisters were prepared at 50% at RH with Ultra Zero air over 3 nonconsecutive days.
- Each preparation was sampled 7+ times at 500 mL.
- 71 of 75 compounds fell below 20pptv.
  - **5.18 pptv** average MDL for 71 compounds.

Compound	MDL Spike
Propene	9.53
1,3-Butadiene	5.41
Benzene	3.80
Trichloroethene	2.45
Toluene	6.77
Tetrachloroethene	2.67
Styrene	1.19
Naphthalene	8.36

# Instrument qualification

## Instrument detection limit challenge at 5pptv

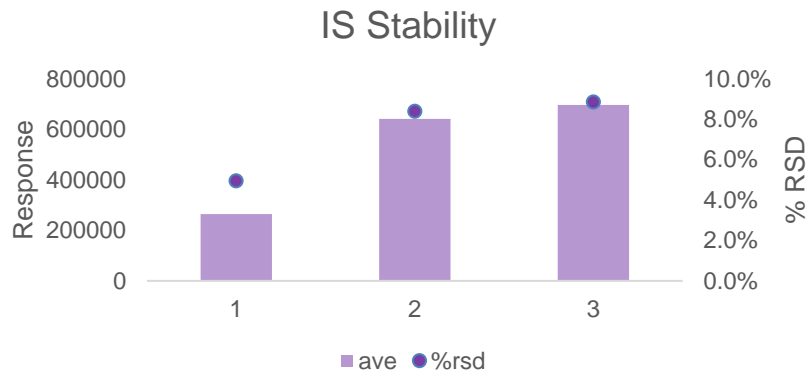
- Canister prepared at 100pptv, sampling 25mL for 5pptv concentration.
- Challenge focused on instrument by alleviating CWEG background
- **1.64 pptv** average IDL for all 75 compounds.
- There's no "I" in CWEG!



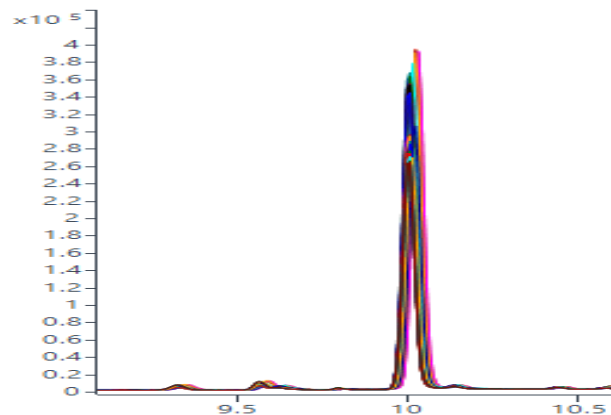
# Instrument qualification

## Stable results over time

- Recovery of IS
  - 36 runs over 3 weeks
  - 4.9% RSD Bromochloromethane
  - 8.4% RSD 1,4-Difluorobenzene
  - 8.8% RSD Chlorobenzene-d5



- Stability of RT
  - 36 runs over 3 weeks
  - 0.65% average STD across 75 compounds



36 repeats over 3 weeks

# Ambient canister samples

## Real-world canister analysis

- Running “grab” samples **without dilution** helps alleviate CWEG.
  - Diluent gas (G) and connections (E) eliminated
- Multiple samples possible from unpressurized 6-liter canisters.
  - 4 x 500 mL samples
  - 6x 250 mL samples
- Consistent results from ambient pressure to approx. -13 in Hg.

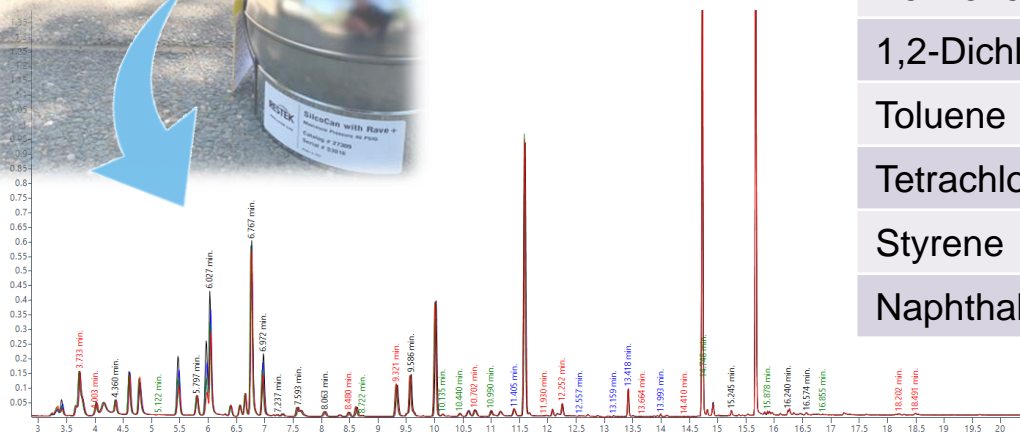


Blue trace – indoor air, office space; black trace – outdoor air, parking lot



# Ambient canister samples

500 mL sampled 4 times from unpressurized canister

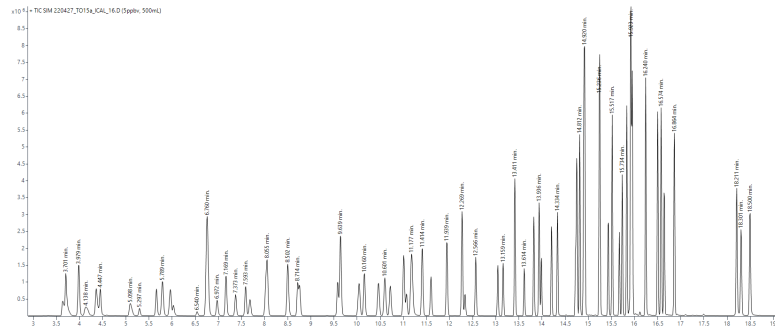


Compound	Ave (pptv)	% RSD
Propene	198.91	0.51%
FR-12	459.08	0.31%
Chloromethane	413.19	1.93%
Benzene	50.30	0.65%
1,2-Dichloroethane	11.29	2.57%
Toluene	109.81	1.39%
Tetrachloroethene	4.26	2.85%
Styrene	5.84	2.11%
Naphthalene	8.46	7.03%

# Summary

Discover more – Deliver more

- ✓ Calibration at extremes of method requirements.
- ✓ Water management with Dry Focus 3.
- ✓ Consistent and reproducible operation results in:
  - ✓ Successful MDL's and ASB's
  - ✓ Low IDL
- ✓ Consistent results from ambient pressure to approx. -13 in Hg.
  - ✓ Reduced vulnerability to CWEG



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