Has the Helium bubble burst?

Using hydrogen carrier gas with Multi-Gas enabled thermal desorption and a novel EI source for TD-GC-MS analysis of standard ambient air monitoring methods

Laura Miles
Markes International

Angela Smith Henry, Amanda McQuay
Agilent Technologies, Inc.

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Trusted Answers

Helium

Helium remains the best carrier gas to use for GC/MS analysis, but…

- Supply shortages are becoming common
- Costs are rising
- Questions about sustainability are being raised

Reasons to use Hydrogen Carrier Gas

- Readily available already used for FID and other detectors)
- Sustainable
- Lower Cost
- Cleans source during use
- Generator options – eliminate cylinders and utilising a cryo-free system
  - Less training required for safety considerations
  - More options for remote or mobile labs which are increasingly required
- Faster analysis
- Lower temperature separation possible
- Move to “more efficient” columns
  - 30 m x 0.25 mm x 0.25 µm → 20m x 0.18 mm x 0.18 µm

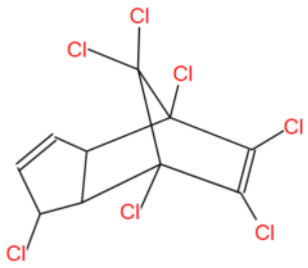
But….

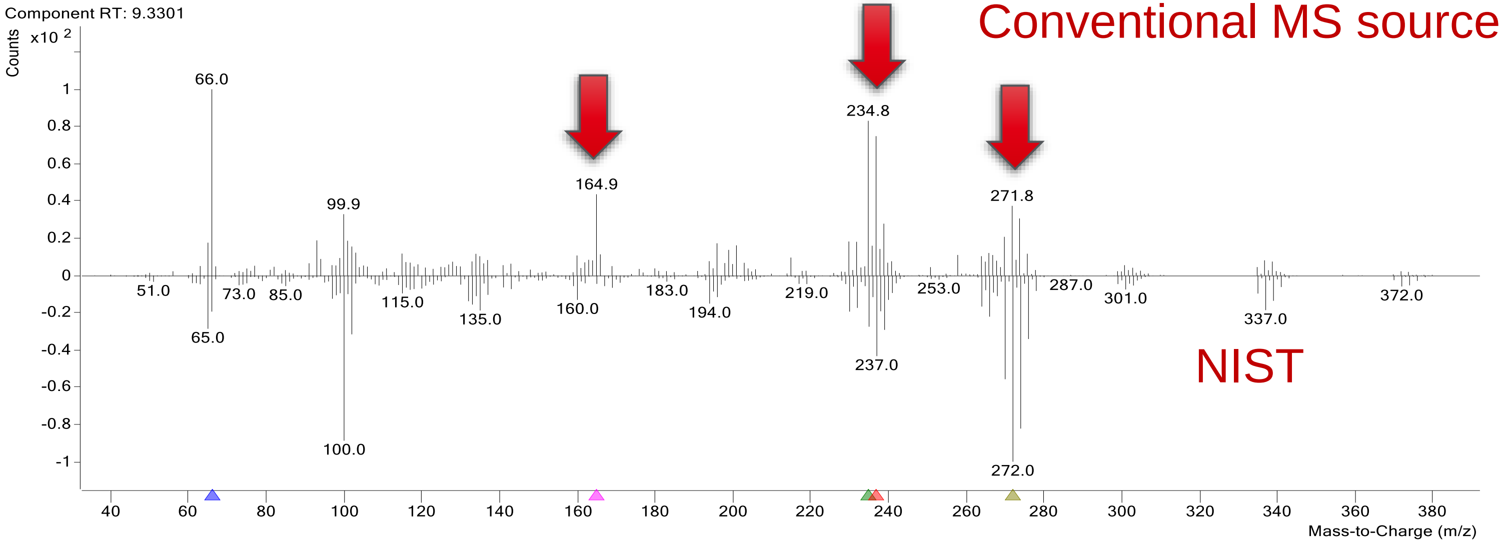
Common problems with H_2 and a normal GC/MS

- Hydrogenation, de-chlorination
- Sensitivity
- Spectral matching
- Safety concerns

Dechlorination with H_2 carrier gas can cause spectra mismatch

Heptachlor





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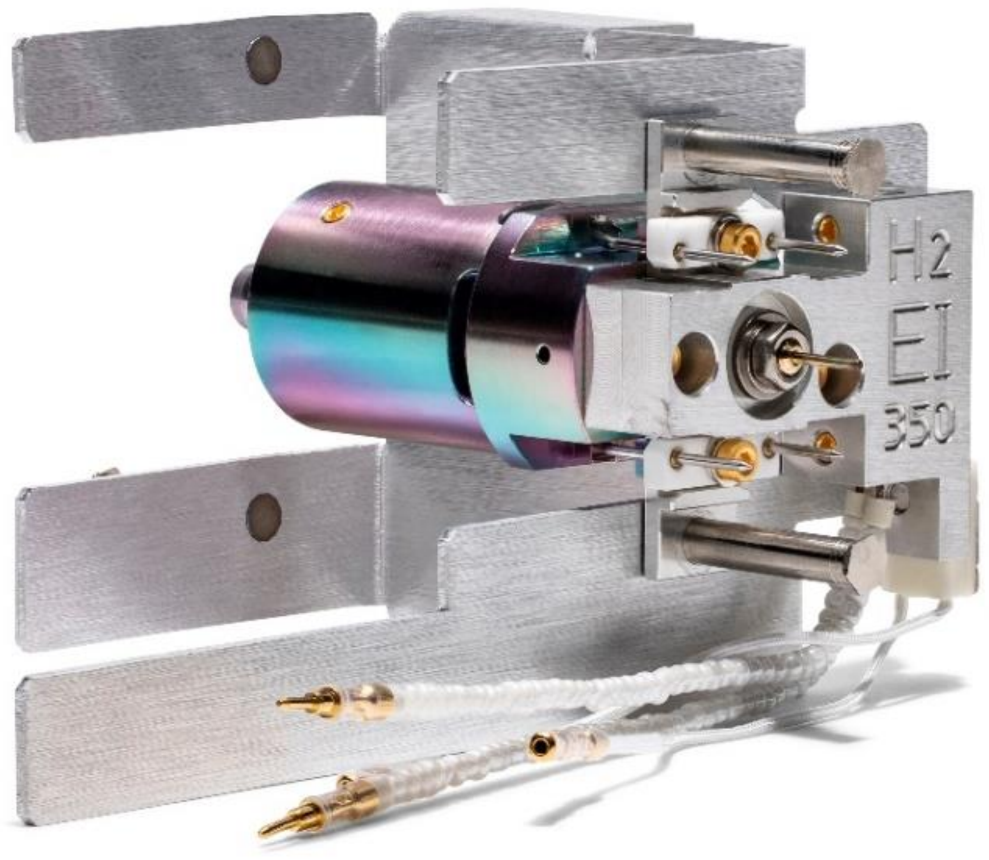
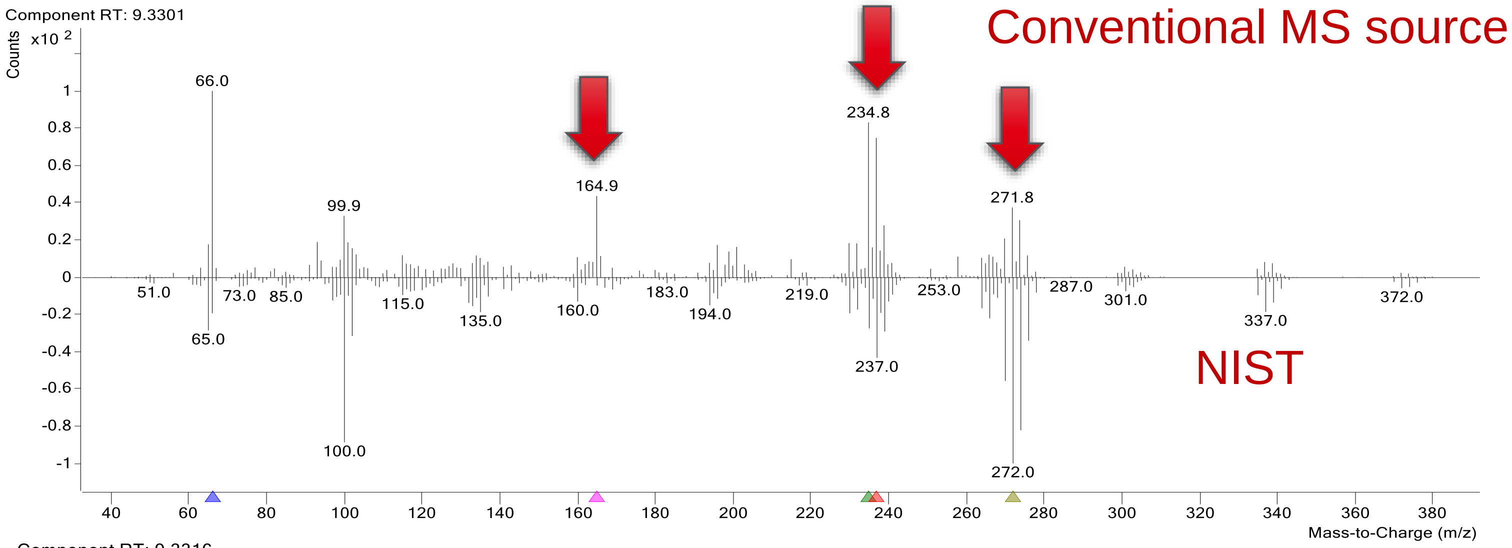
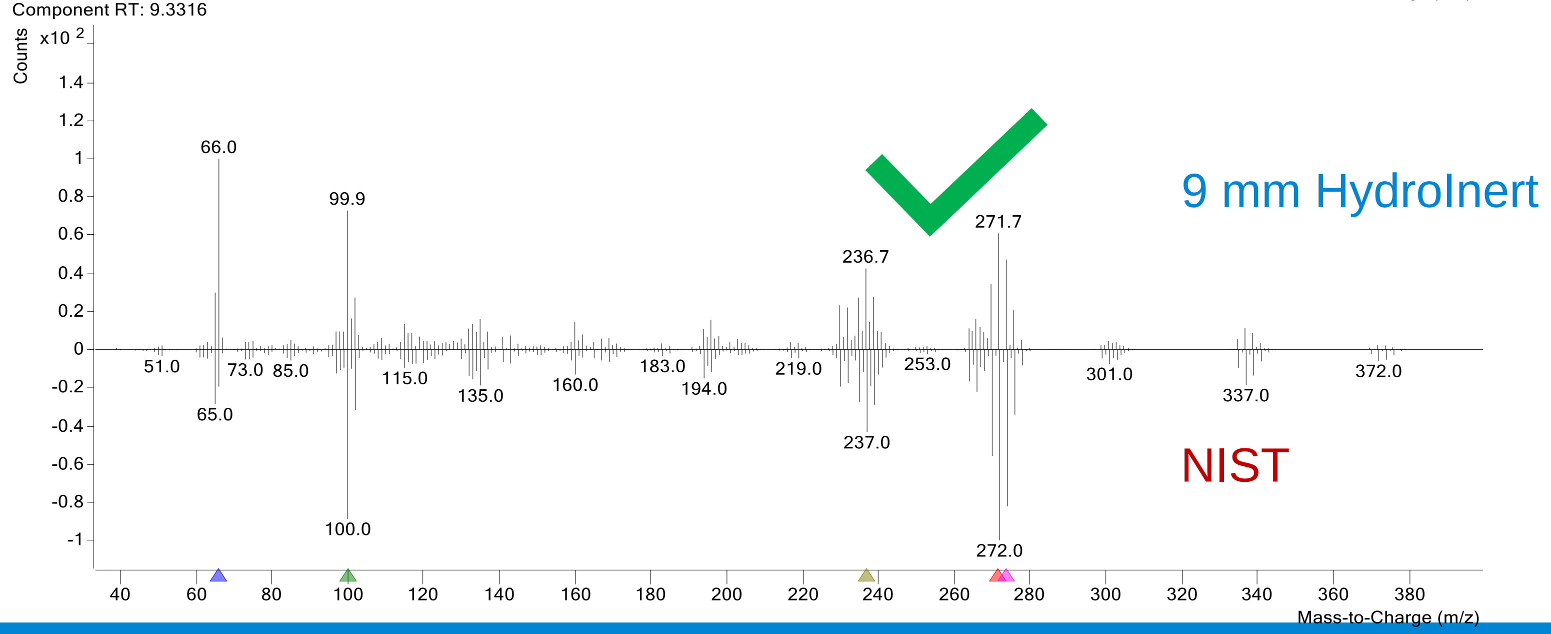
Agilent HydroInert Source for Hydrogen Carrier Gas on GC/MS

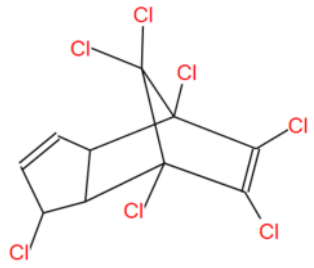


- Allows for the use of Hydrogen Carrier Gas with better supply and reduced cost
- Faster, shorter Separations
- Reduces loss of sensitivity and spectral anomalies
- Reduced source cleanings and maintenance

Heptachlor With H_2 Carrier







Dechlorination with H_2 carrier gas can cause spectra mismatch

HydroInert reduces de-chlorination!

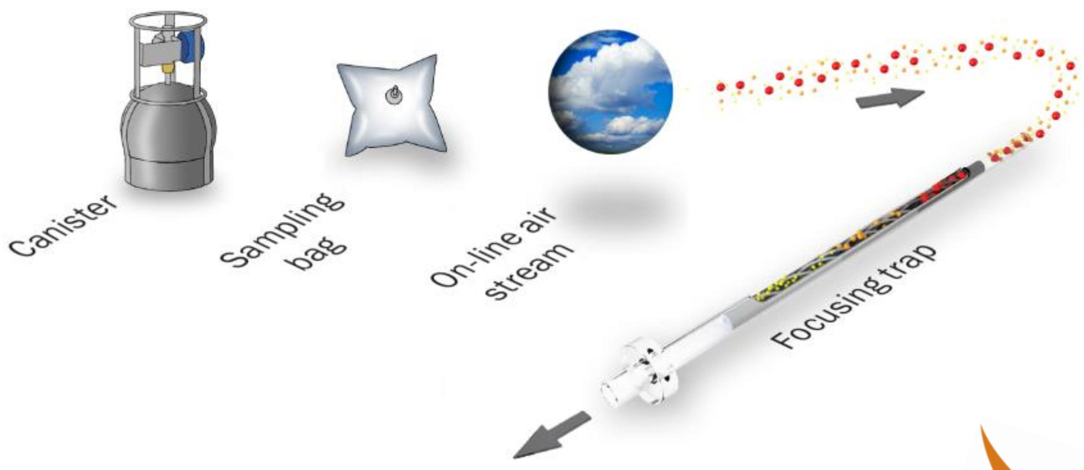
Instrumentation for TO-15 and air toxics analysis with H_2 carrier gas

Multi-Gas TD system with 8890-5977B and HydroInert source

HydroInert source

MULTI-GAS ENABLED

Canister pre-concentration & GC injection with Markes TD



1. Volatiles transferred from canister/bag (or directly from the atmosphere) onto the focusing trap.

2. Focusing trap rapidly heated in a reverse flow of gas. Analytes are desorbed and injected to GC.
    - Optional split

US EPA Method TO-15 by TD-GC-MS
Standard method for analysis of air toxic VOCs

VOCs tested as a measure of ‘air quality’ in industrial and urban environments

Analysis of VOCs covered by many standard methods and regulations

U.S EPA Method TO-15

- Canister sampling
- Management of humid samples up to 100%RH

65 air toxics compounds ranging in volatility from propene to naphthalene, and including polar and non-polar compounds from a range of functional groups

Now, for the first time, hydrogen can be used as carrier gas on fully-certified TD-GCMS systems

Full method compliance can be achieved

Method parameters of the TD-GC/MS system for H_2 carrier gas

Water removal:	
Instrument:	Kori-xr (Markes International)
Trap temperatures:	–30 °C / +300 °C
TD	
Instrument:	UNITY-xr (Markes International)
Flow path:	120 °C
Sample flow:	50 mL/min
Trap purge: Trap desorption:	1.0 min at 50 mL/min 2.0 min at 4 mL/min split flow
Cold trap:	‘Air toxics’ (part no. U-T15ATA-2S)

Canister sampling:	
Instrument:	CIA Advantage-xr (Markes International)
Sample volume:	Up to 400 mL (for samples of 50–100% RH)

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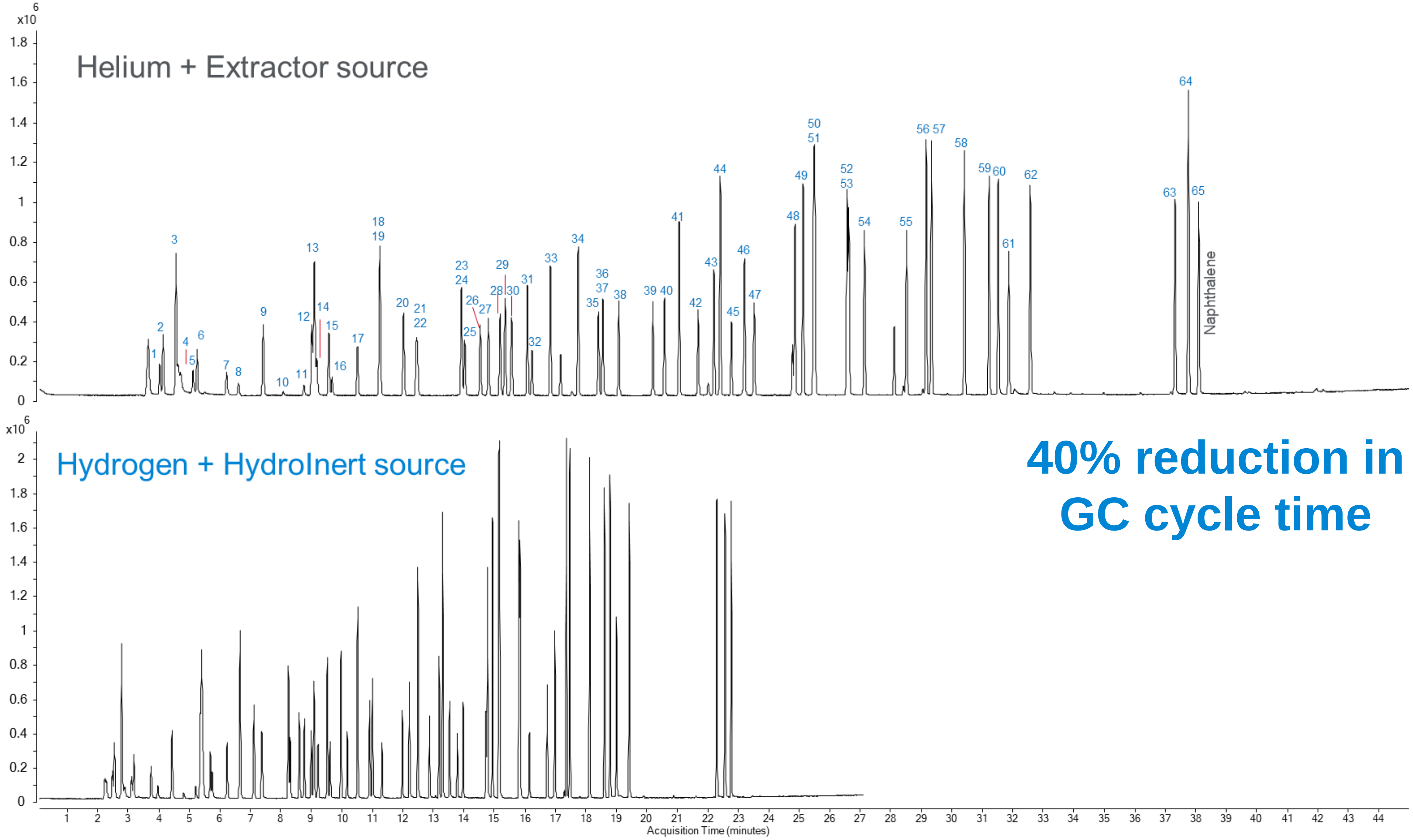
Parameter	Value
Gas chromatograph	Agilent 8890B GC
Column	Agilent J&W DB-624, 60 m × 0.25 mm × 1.40 µm (p/n: 123-1364)
Inlet	Splitless
Inlet temperature	120 °C
Oven temperature program	30 °C (3 min) 8.3 °C/min to 230 °C (0 min)
Total run time	27 min
MS transfer line temperature	230 °C
Carrier gas	Hydrogen, 2.0 mL/min constant flow
MS parameters	
Source	HydroInert source
Lens	6mm HydroInert
Mode	Electron ionization, 70 eV
Source temperature	300 °C
Quadrupole temperature	200 °C
Scan range	m/z 30–300

Comparing Helium and Hydrogen Chromatography

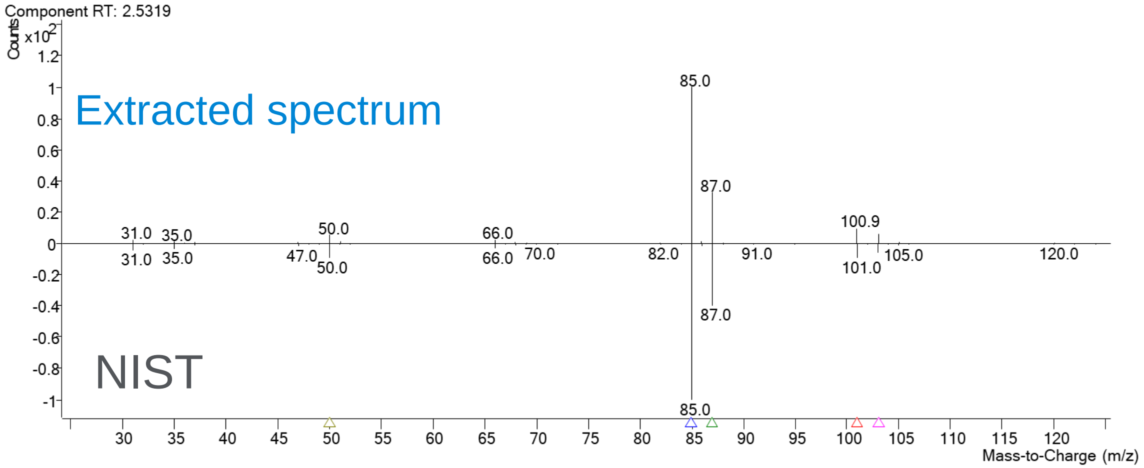


40% reduction in GC cycle time

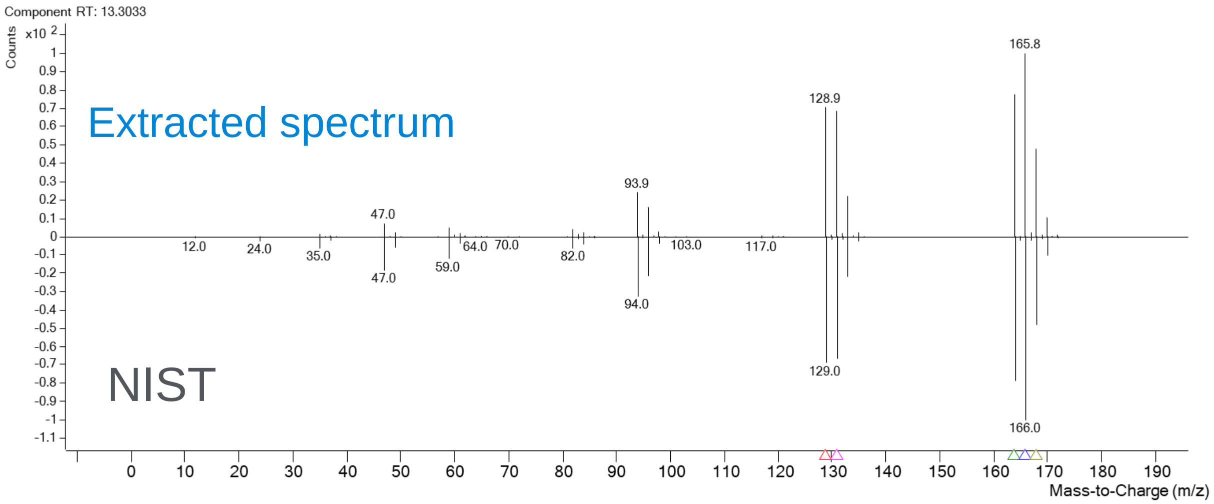
Retain your mass spectral fidelity and library match scores

High library match scores (to helium libraries) with H_2 carrier gas and HydroInert source

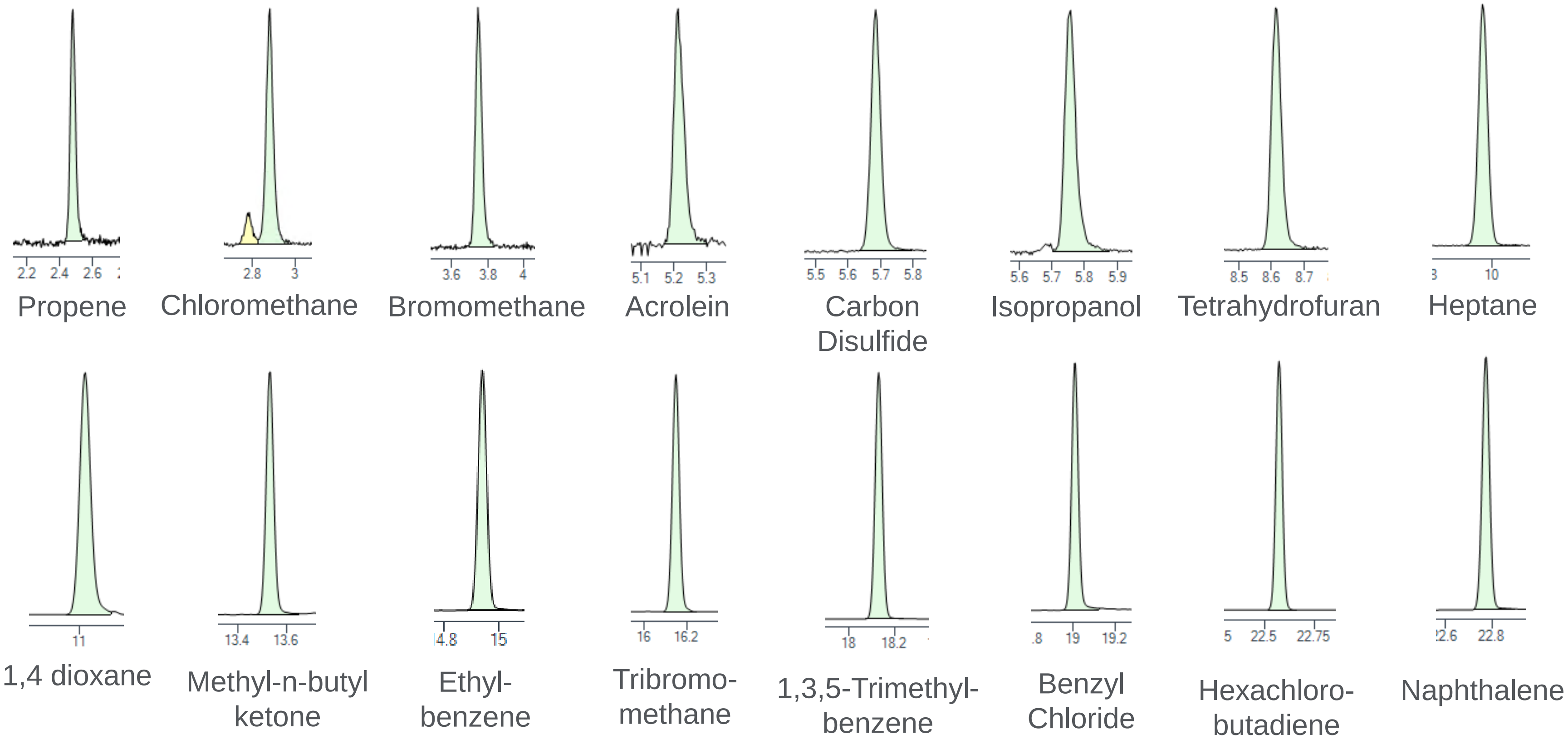
Dichlorodifluoromethane: LMS = 97.5



Tetrachloroethylene: LMS = 98.8



Chromatography: Peak Shape in H_2 carrier gas with TD-GC/MS and HydroInert source



Retain excellent Gaussian peak shape across the TIC

Quantitative results

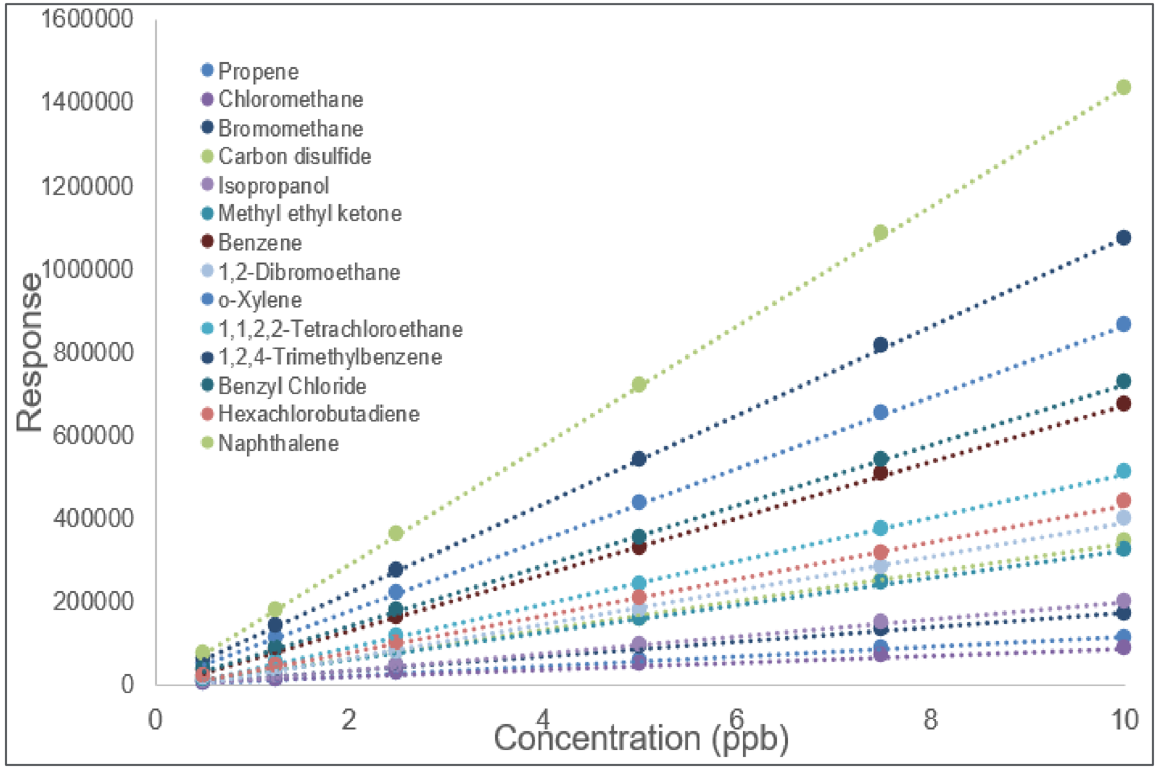
Compound	Linearity	%RSD RRF of calibration	%RSD Response (N=10)	%RSD Retention time (N=50)	Method detection limits (ppb)
Average across full range of target VOCs	0.999	7.47%	1.22%	0.09%	0.052
Criteria	0.99+	<30%	<20%	<1%	<0.5

Excellent linearity, with average R^2 of 0.999.

Average relative response factor RSD=7.5%, all analytes below 30%

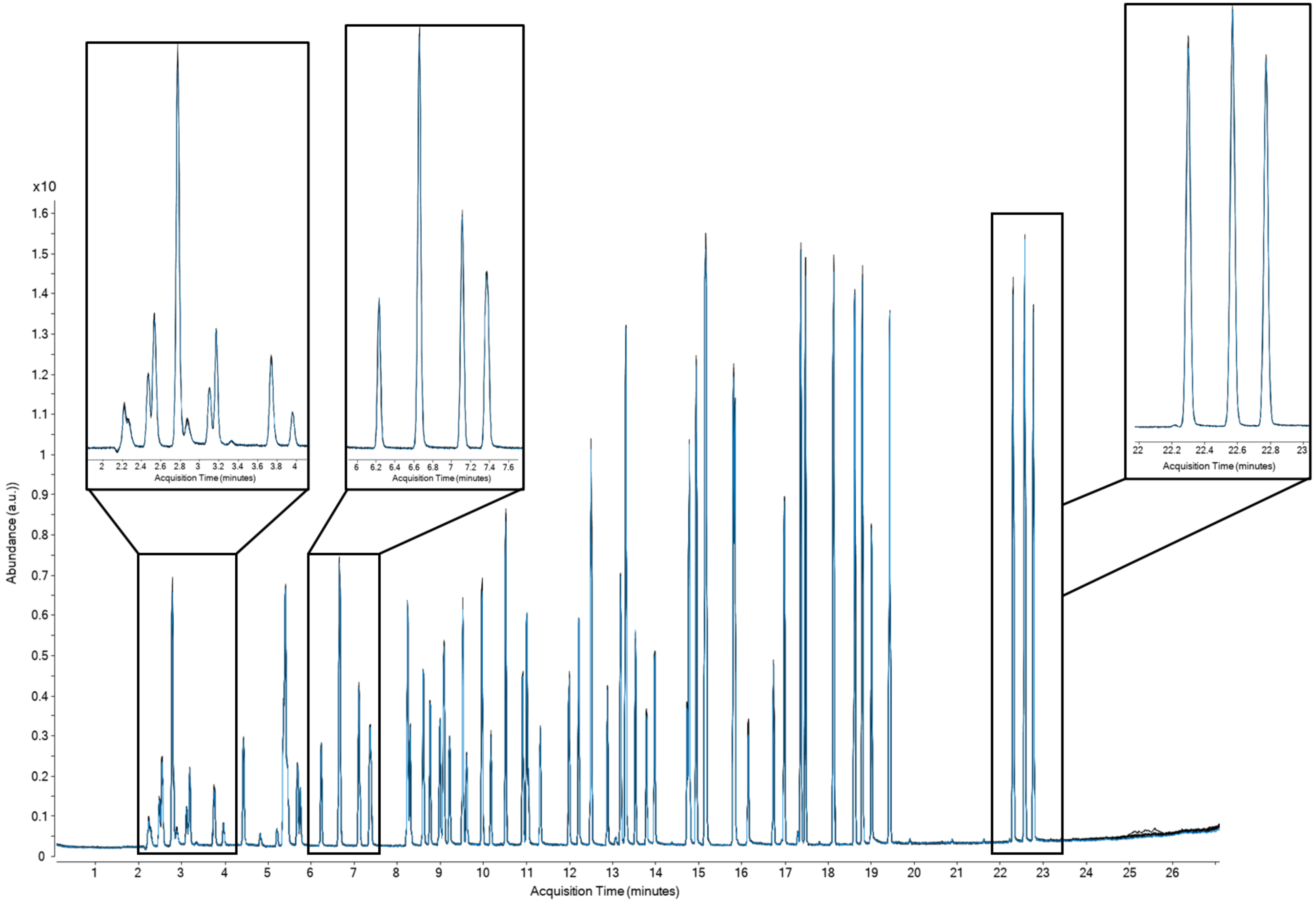
Average area RSD =1.22% (n=10 replicates of 10 ppb 100%RH)

Average retention time RSD=0.09% (n=50)



Excellent reproducibility with H_2 carrier gas

10 overlaid replicates



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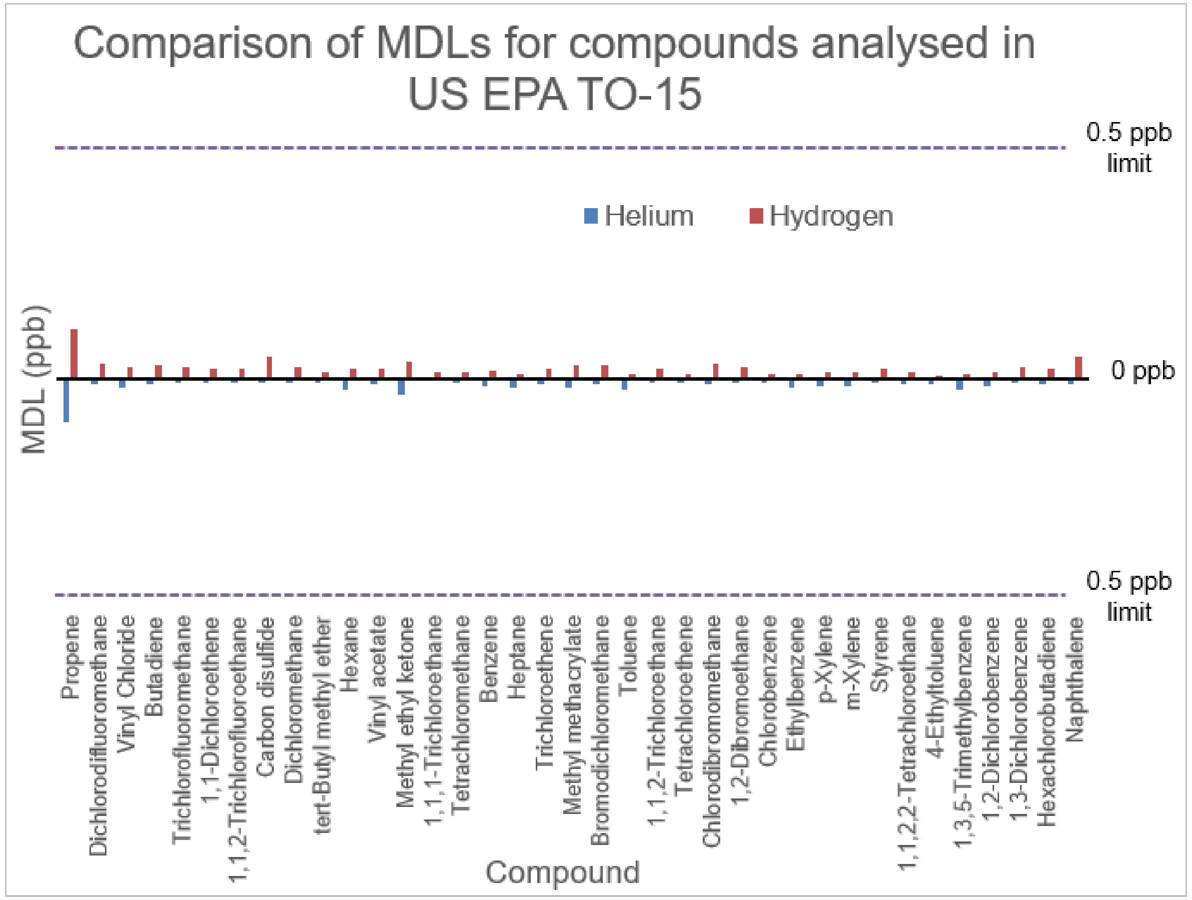
What about sensitivity with hydrogen carrier gas?
> Method compliance achieved



	Compound	Hydrogen MDL (ppv)
1	Propene	113
2	Dichlorodifluoromethane	38
3	Vinyl Chloride	29
4	Butadiene	33
5	1,1-Dichloroethene	24
6	1,1,2-Trichlorofluoroethane	25
7	Carbon disulfide	53
8	Dichloromethane	29
9	tert-Butyl methyl ether	16
10	Vinyl acetate	23
11	Methyl ethyl ketone	42
12	Tetrachloromethane	17
13	Benzene	19
14	Heptane	13
15	Methyl methacrylate	34
16	Bromodichloromethane	34
17	Toluene	14
18	Tetrachloroethene	13
19	1,2-Dibromoethane	28
20	Chlorobenzene	14
21	Ethylbenzene	14
22	Styrene	23
23	1,1,2,2-Tetrachloroethane	16
24	4-Ethyltoluene	11
25	1,3,5-Trimethylbenzene	14
26	1,2-Dichlorobenzene	17
27	Hexachlorobutadiene	23
28	Naphthalene	50
	Average	28

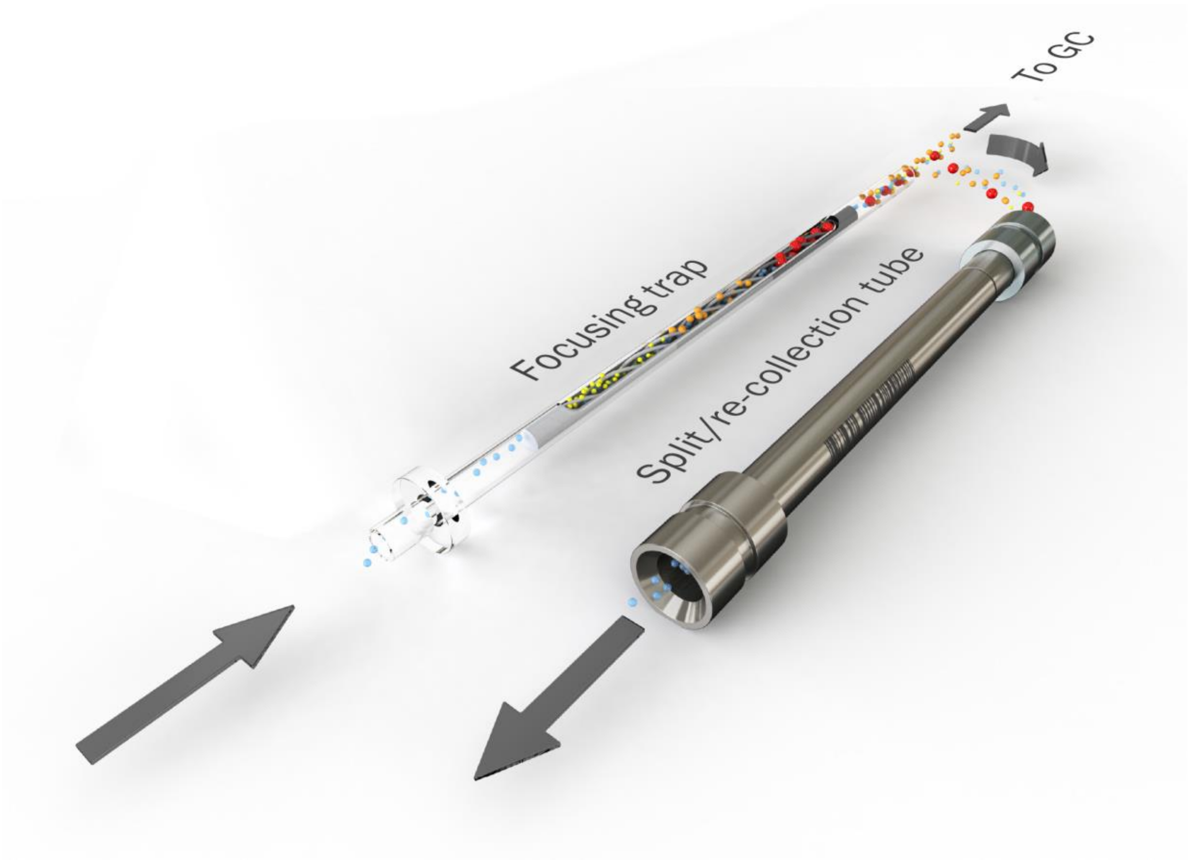
Do we see any hydrogenation?

A simple, automated validation procedure using re-collection

During trap desorption the split portion of the sample can be collected onto a sorbent tube, this is known as re-collection.

This tube can then be analysed and the split portion collected again.

This process is repeated several times, known as a re-collection series.

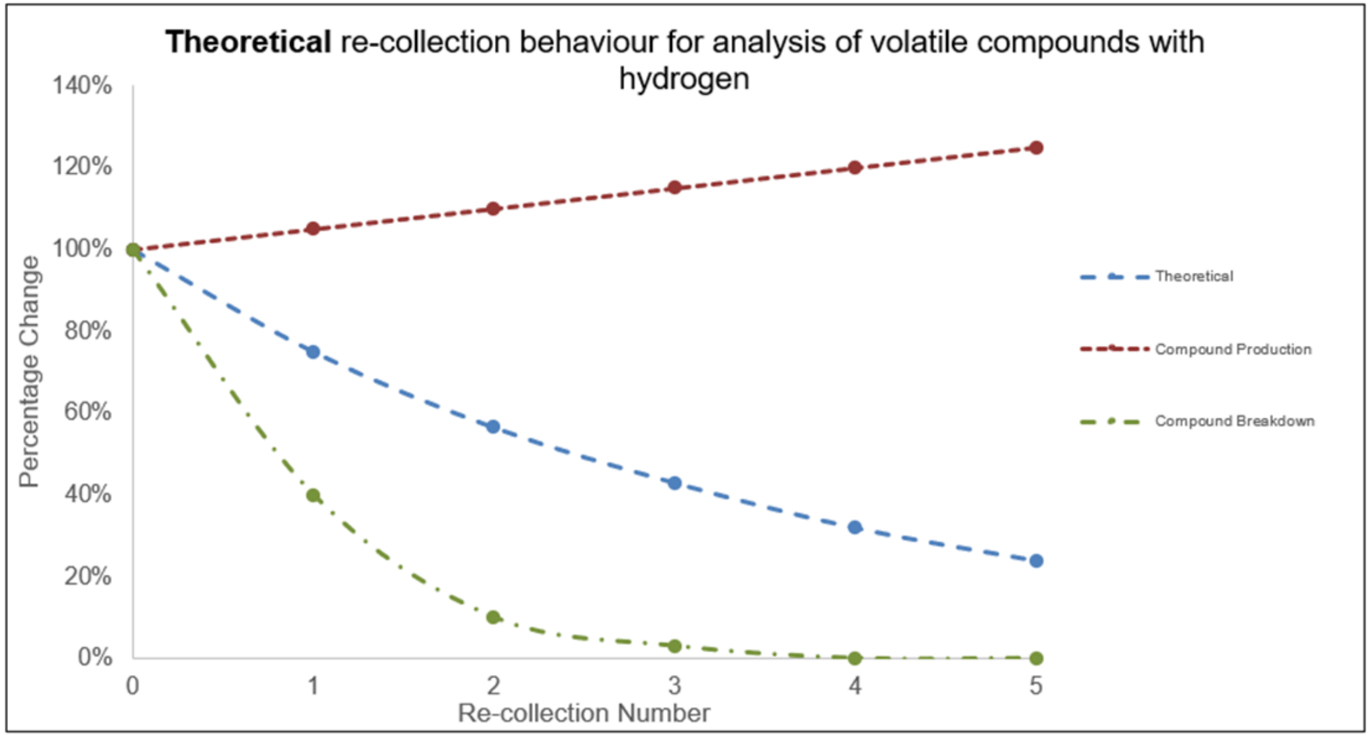


Do we see any hydrogenation?

A simple, automated validation procedure using re-collection

A re-collection series can be used to validate a method and check for degradation, or hydrogenation, in the thermal dersorber.

- Theoretical analyte response decays across the re-collection series based on split ratio
- Any degraded compounds will drop much faster than theoretical
- By products of degradation / hydrogenation will increase



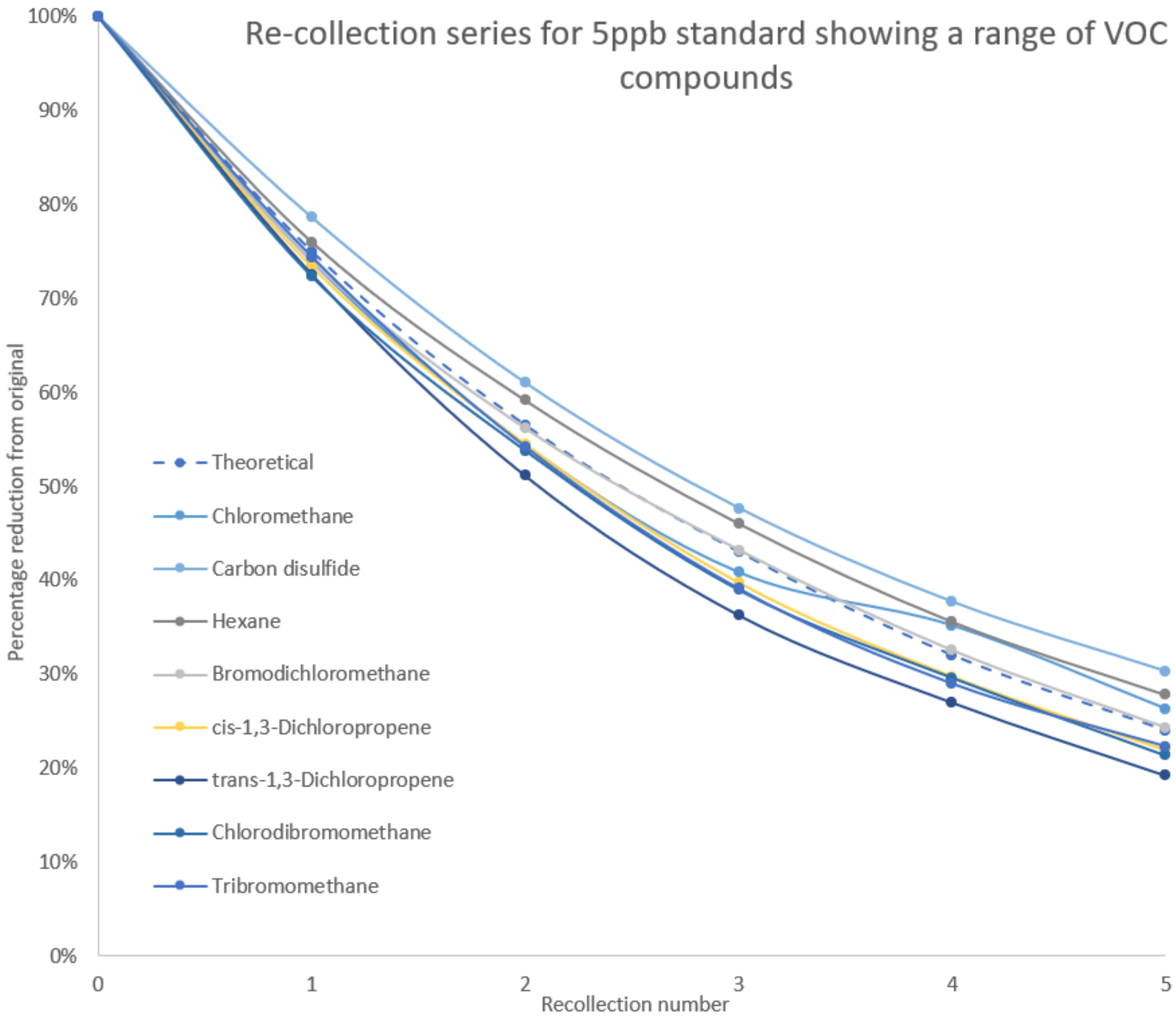
Do we see any hydrogenation?

A simple, automated validation procedure using re-collection

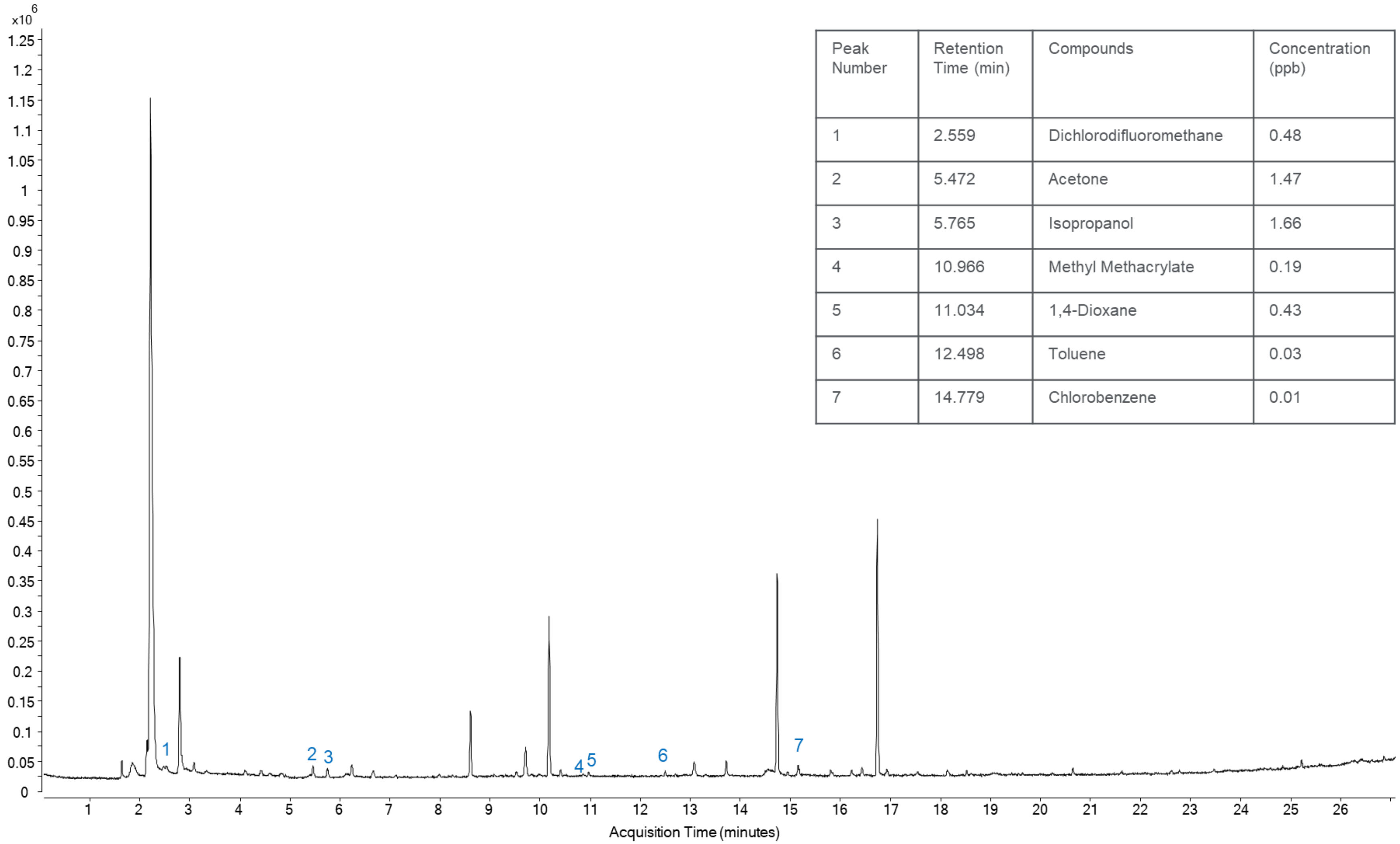
TO-15 compounds follow the theoretical trend across the re-collection series

A simple, quick way to validate TD based methods.

No breakdown or creation of compounds with H_2 carrier and HydroInert source!



Testing real world air samples with H_2 TD-GC/MS and HydroInert Source



Peak Number	Retention Time (min)	Compounds	Concentration (ppb)
1	2.559	Dichlorodifluoromethane	0.48
2	5.472	Acetone	1.47
3	5.765	Isopropanol	1.66
4	10.966	Methyl Methacrylate	0.19
5	11.034	1,4-Dioxane	0.43
6	12.498	Toluene	0.03
7	14.779	Chlorobenzene	0.01

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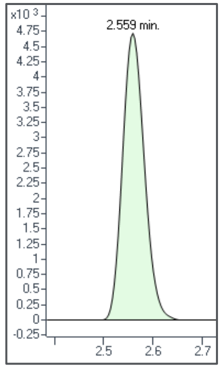
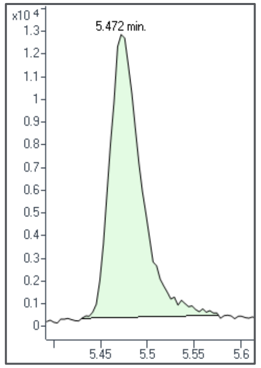
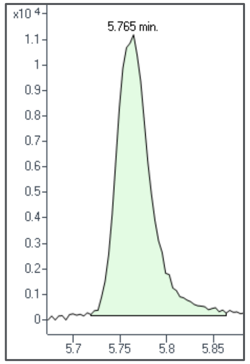
Testing real world air samples with H2 TD-GC/MS and HydroInert Source



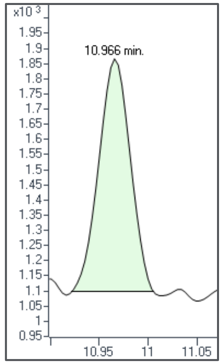
Dichlorodifluoromethane



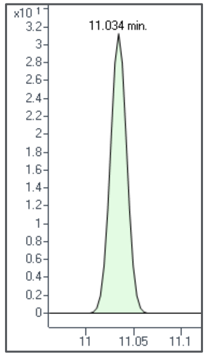
Acetone



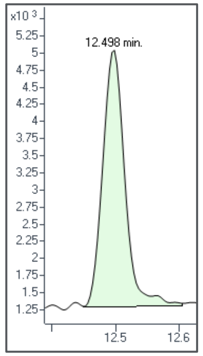
Isopropanol



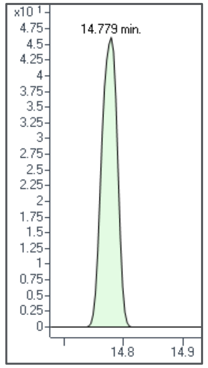
Methyl Methacrylate



1,4-Dioxane



Toluene



Chlorobenzene

Retain good peak shapes for a real world sample

Extend this method compliance with sorbent tubes methods as well

TO-15 + TO-17 on the same system

US EPA Method TO-17
US EPA Method 325
China HJ 644
ISO 16000-6
ISO 16017-1 & 2

MULTI-GAS ENABLED

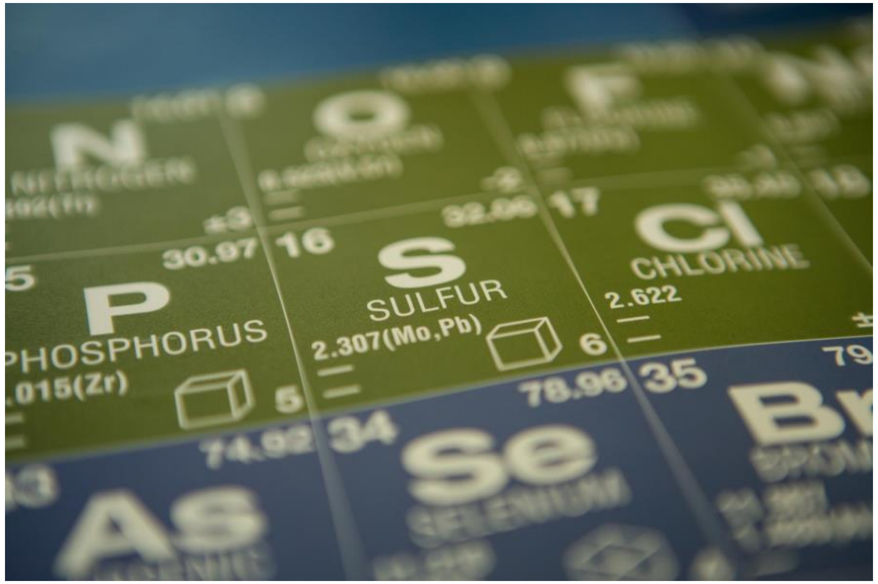
US EPA Method TO-15
China HJ 759
China 117 Method

Going beyond method compliance

Can we challenge the Multi-Gas TD with HydroInert source GC/MS system with other difficult ambient air compounds, such as sulfurs or aldehydes?

Researchers are adding these compounds to the same suite of air toxics, including:

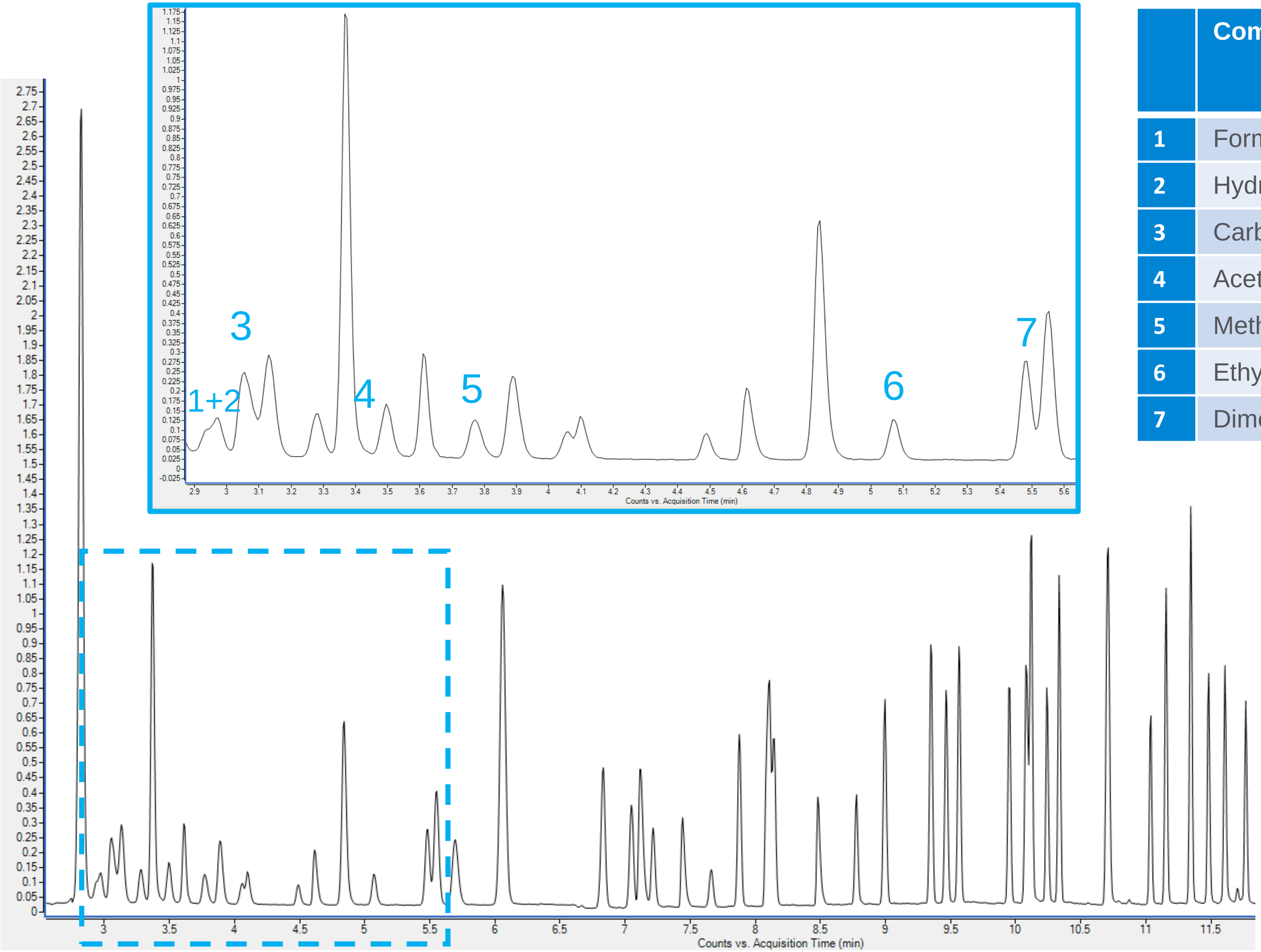
- Hydrogen sulfide
- Methyl mercaptan
- Carbonyl sulfide
- Ethyl mercaptan
- Dimethyl sulfide
- Formaldehyde
- Acetaldehyde



- The sulfur compounds are important because they are responsible for malodours which can lead to complaints from anyone living nearby specific sites, and aldehydes because of concerns over their detrimental effects on humans over extended time periods

Going beyond method compliance:

TIC m/z 30-350 containing air toxics including sulfurs and aldehydes on the same system

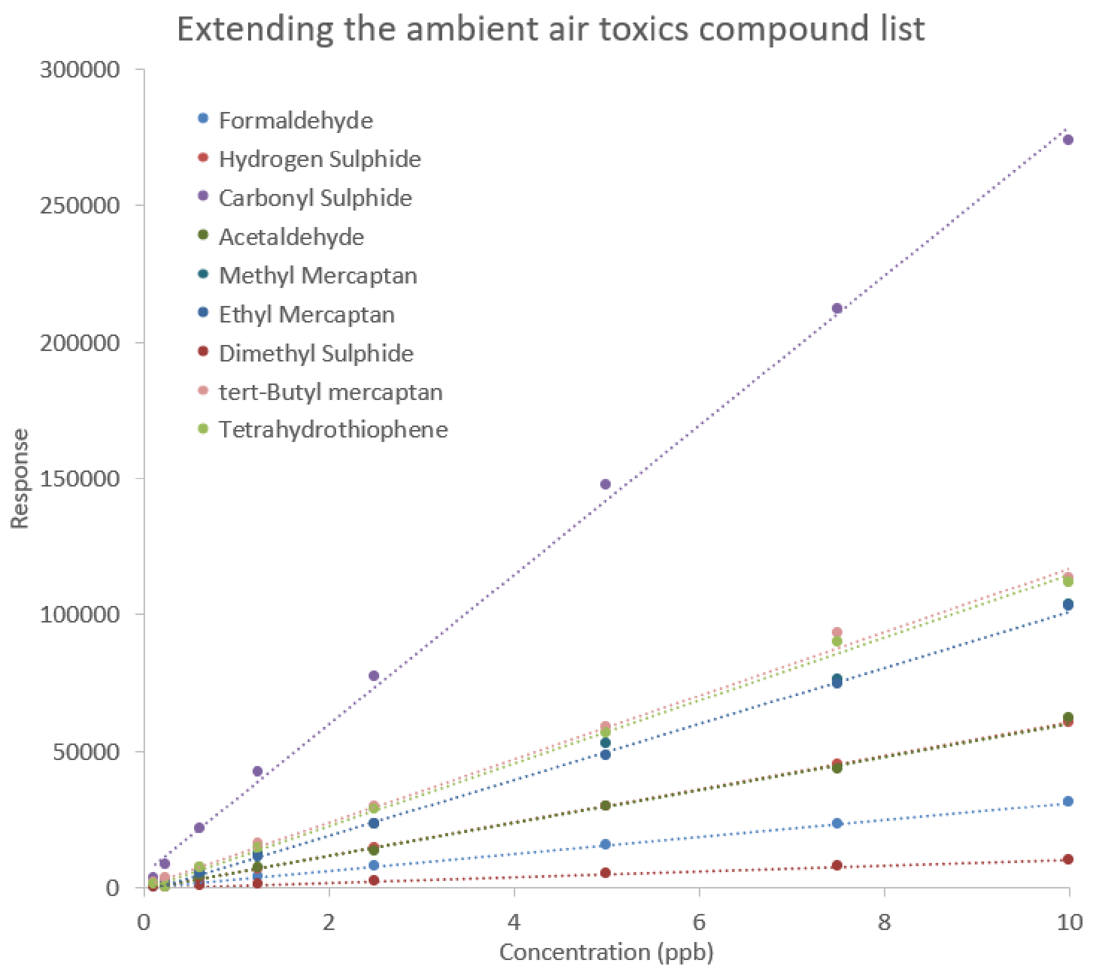


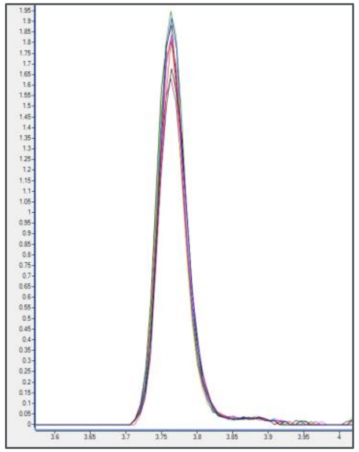
	Compound	Retention time	R^2 (0.125-10 ppb)	RSD% (n=10) 10ppb	RT RSD % (n=10)
1	Formaldehyde	2.94	0.9980	2.20	0.07
2	Hydrogen Sulphide	2.94	0.9997	1.51	0.11
3	Carbonyl Sulphide	3.08	0.9979	0.89	0.11
4	Acetaldehyde	3.40	0.9981	3.80	0.09
5	Methyl mercaptan	3.78	0.9923	1.30	0.09
6	Ethyl mercaptan	5.05	0.9999	1.72	0.04
7	Dimethyl sulphide	5.45	0.9998	2.16	0.06

H_2 carrier gas

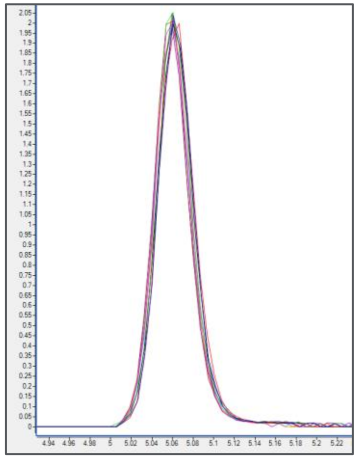
Multi-gas TD-GC/MS with HydroInert source

Going beyond method compliance

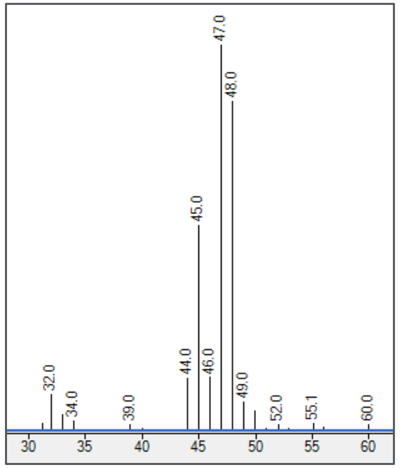


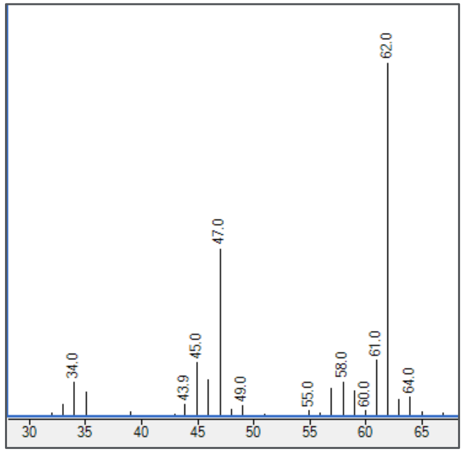


Methyl mercaptan
EIC m/z 47



Ethyl mercaptan
EIC m/z 62





Summary

For the first time, hydrogen can be used as carrier gas on fully-certified TD-GCMS systems with HydroInert source and Markes Multi-Gas TD system

- Full method compliance can be achieved
- Extend analysis into sulfurs or aldehydes

MULTI-GAS ENABLED

Thank you!

Any Questions?