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Dynamic Focusing:

A New Technique for Focusing VVOC's and Managing Water in Automated Ambient Air Analysis Using TD-GCMS

So what is “Focusing”?

- Focusing is concentration or enrichment of a sample shortly before it is introduced to the GC column. Focusing is also known as ‘trapping’.

- Focusing is used in many environmental GC-based methods, including those for air (TO-15, TO-17, 325B thermal desorption (TD) methods) and water (524/624/8260 purge & trap methods)

- Focusing is needed when the flow from the sample introduction device (TD or P&T) exceeds the column flow; TD, desorption flows are usually 10-50 mL/min, but capillary GC’s prefer 1-2 mL/min

Is “Focusing” always needed?

- No, you don’t have to focus: if a ~50:1 split is used, the sample can go directly to the GC column and in a relatively short time, but it costs sensitivity.

- Peak shapes of VVOC’s can also be poor since the ’injection’ is relatively slow (by VVOC standards)

- This high-split solution may still introduce a lot of water to the column, if the sample was from a humid source

The one-step high split approach results in reduced sensitivity and is unable to manage water; focusing is needed

How does Focusing work?

- The sample, either trapped on a sorbent (in a TD tube) or purged from a vial (P&T) is sent to another tube (‘focusing trap’) filled with one or more sorbents
- The sorbents are normally chosen to match the targeted list of compounds in a method, and may or may not be the same as those in the TD tube
- Ideally, the analytes are held or ‘trapped’ there, and un-needed desorption gas (and hopefully water) flow away from the trap and to exhaust

What Happens Next?

- After this transfer, the focusing trap is then rapidly heated, at a low split or no split at all, and the contents are transferred to the GC capillary column at typical flows (1-2 mL/min)

- The key to successful focusing is to a) gather **all** the analytes of interest and b) introduce them quickly to the column in a ‘plug injection’

This is a two-step approach: sample to focusing trap, focusing trap to column. Although split-less injection is possible, a low split (3:1 or 10:1) is commonly used in at least one of the two steps

What is Static Focusing?

- The process described previosly ***is*** Static Focusing: the analytes are moved to the trap and are held in place there, usually for a few minutes (or longer)

- Because the analytes are held in place inside the trap until the trap is heated, we coined the term “Static Focusing”

- They can be held in place physically on an inert substrate, such as glass beads or wool using low temperatures, with LN_2, or LCO_2 for low boiling point “VVOC’s”

What is Static Focusing?

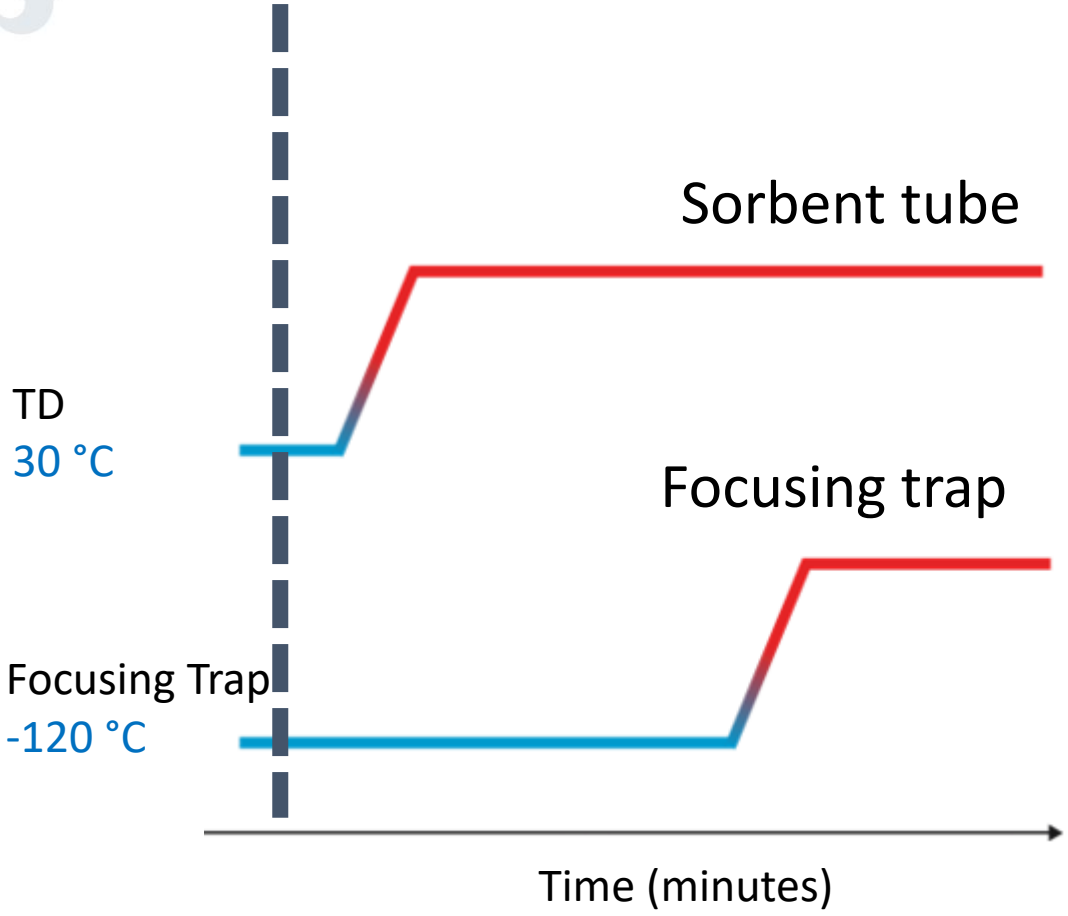
- Alternately, they can be held in place chemically, using one or more sorbents; two or three sorbents are common to deliver a larger BP range of analytes trapped

- Either approach has issues: either the cost and time spent with cryogens, or the need to match the sorbents to the analytes trapped (e.g., targeted analysis only)

- Both have issues with water or solvent: at very low temps on glass beads, water or solvents are literally frozen in place

- To get low BP VVOC's on a sorbent trap, water is retained on molecular sieves commonly used, and this water creates the "*solvent effect*" – an irreproducible pressure pulse that alters the split ratio (and not equally across the range)

Static Focusing – Start



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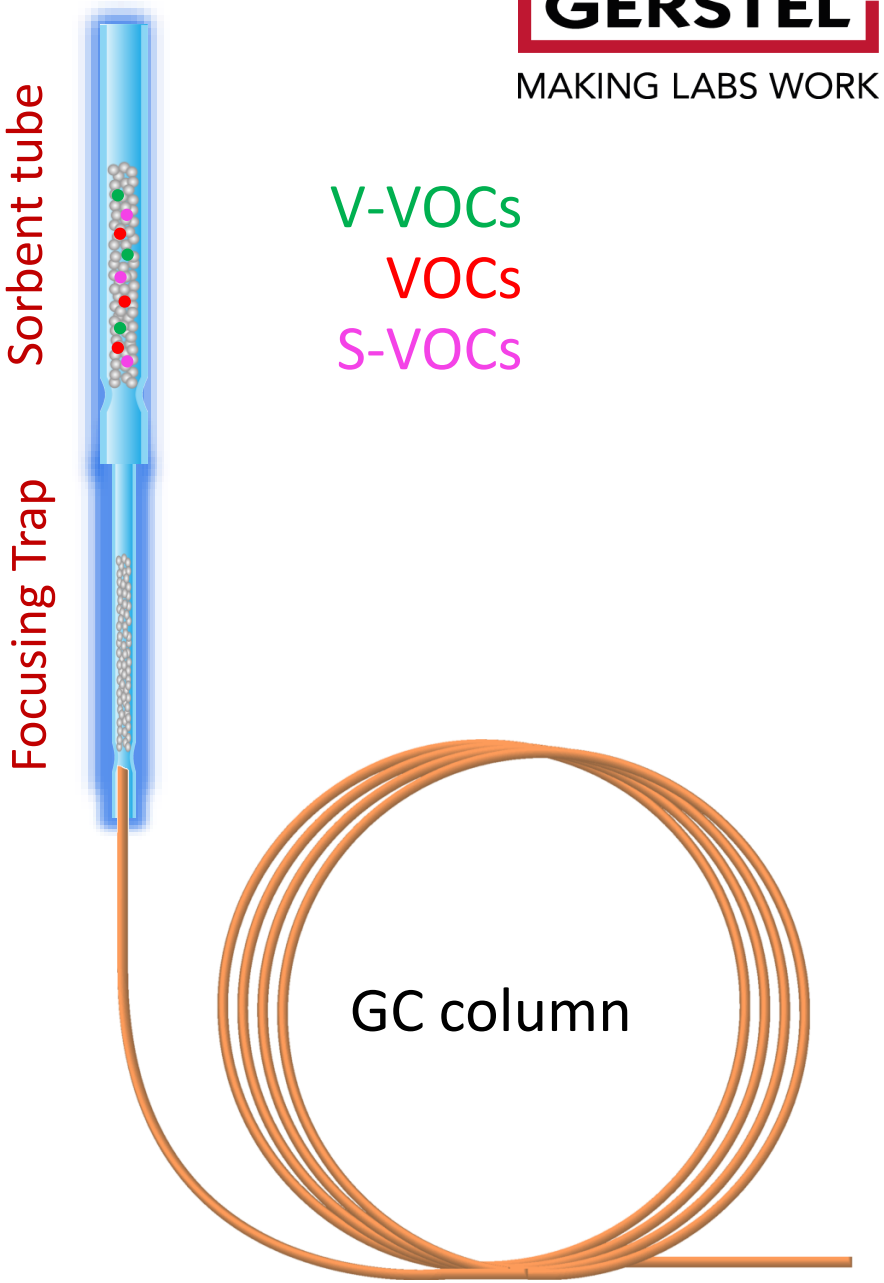
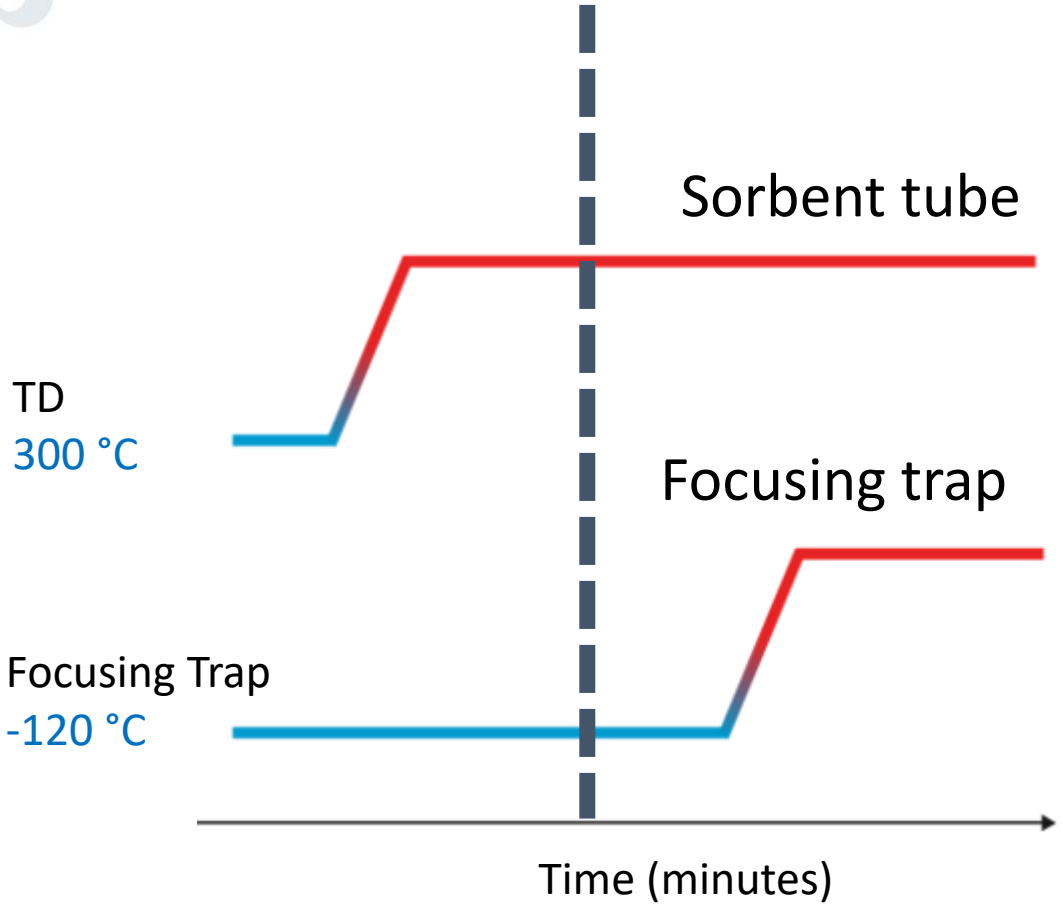
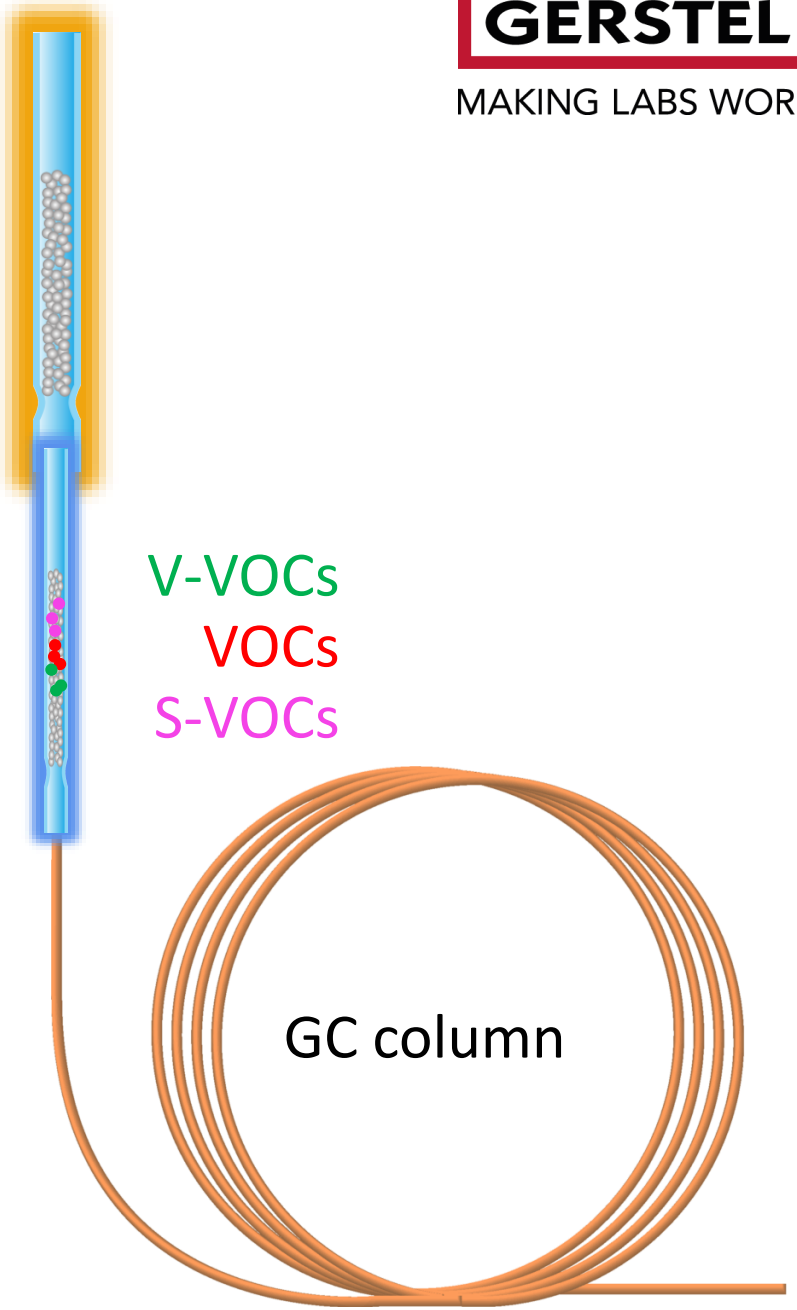
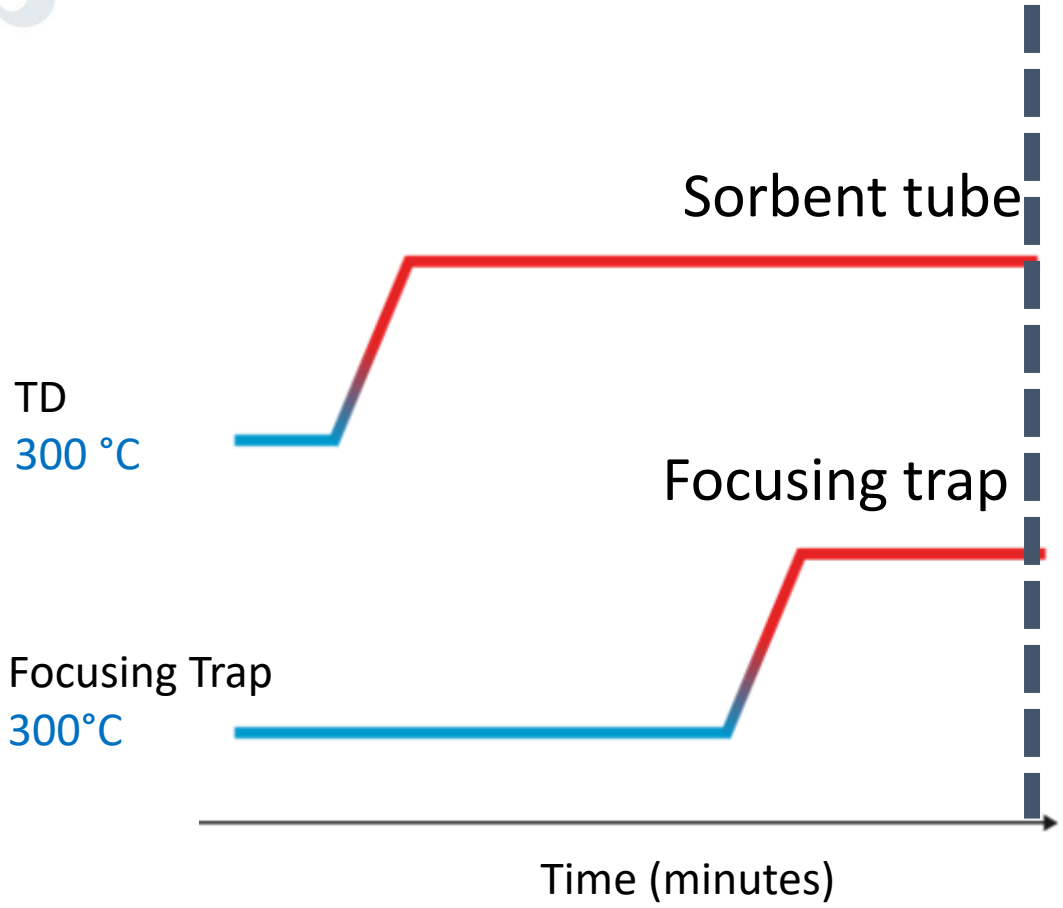


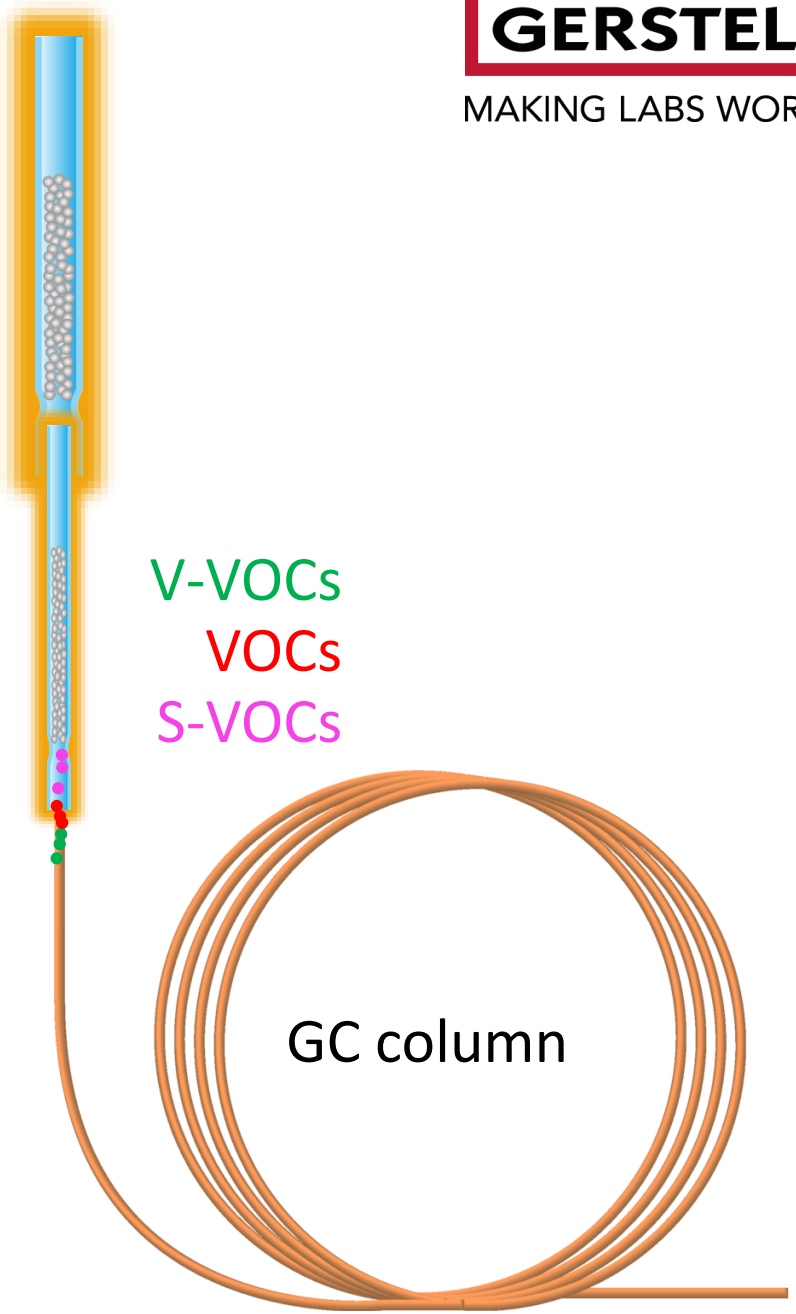
Static Focusing – Step One
Rapid Tube Heat





Static Focusing – Step Two
Rapid Trap Heat





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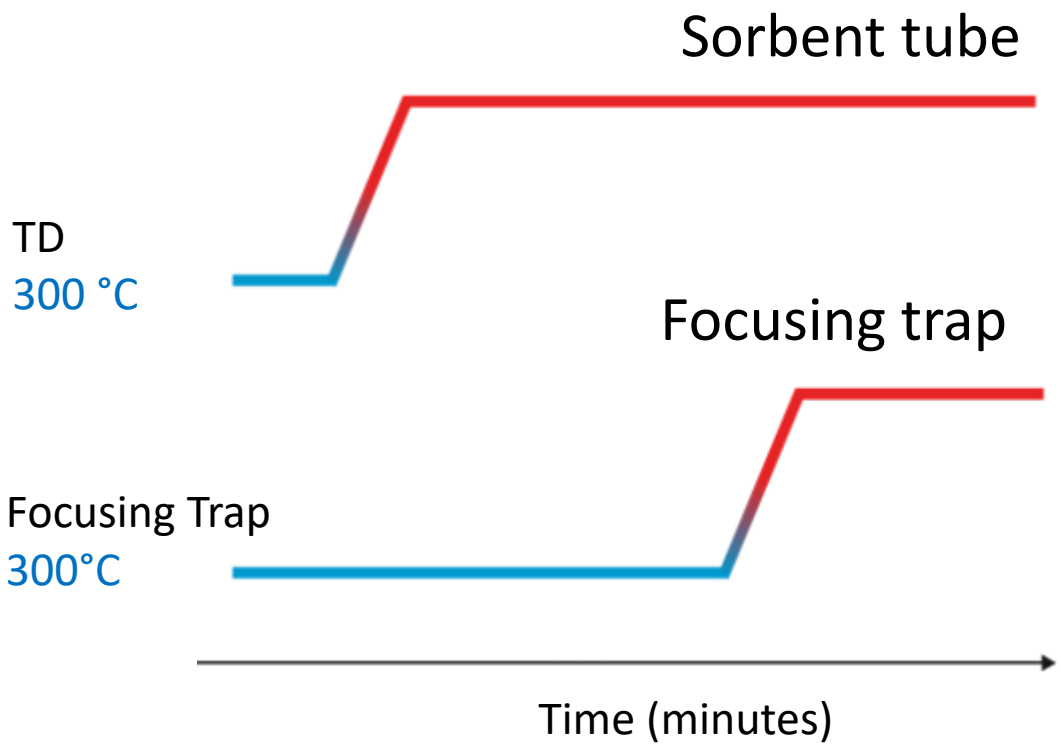
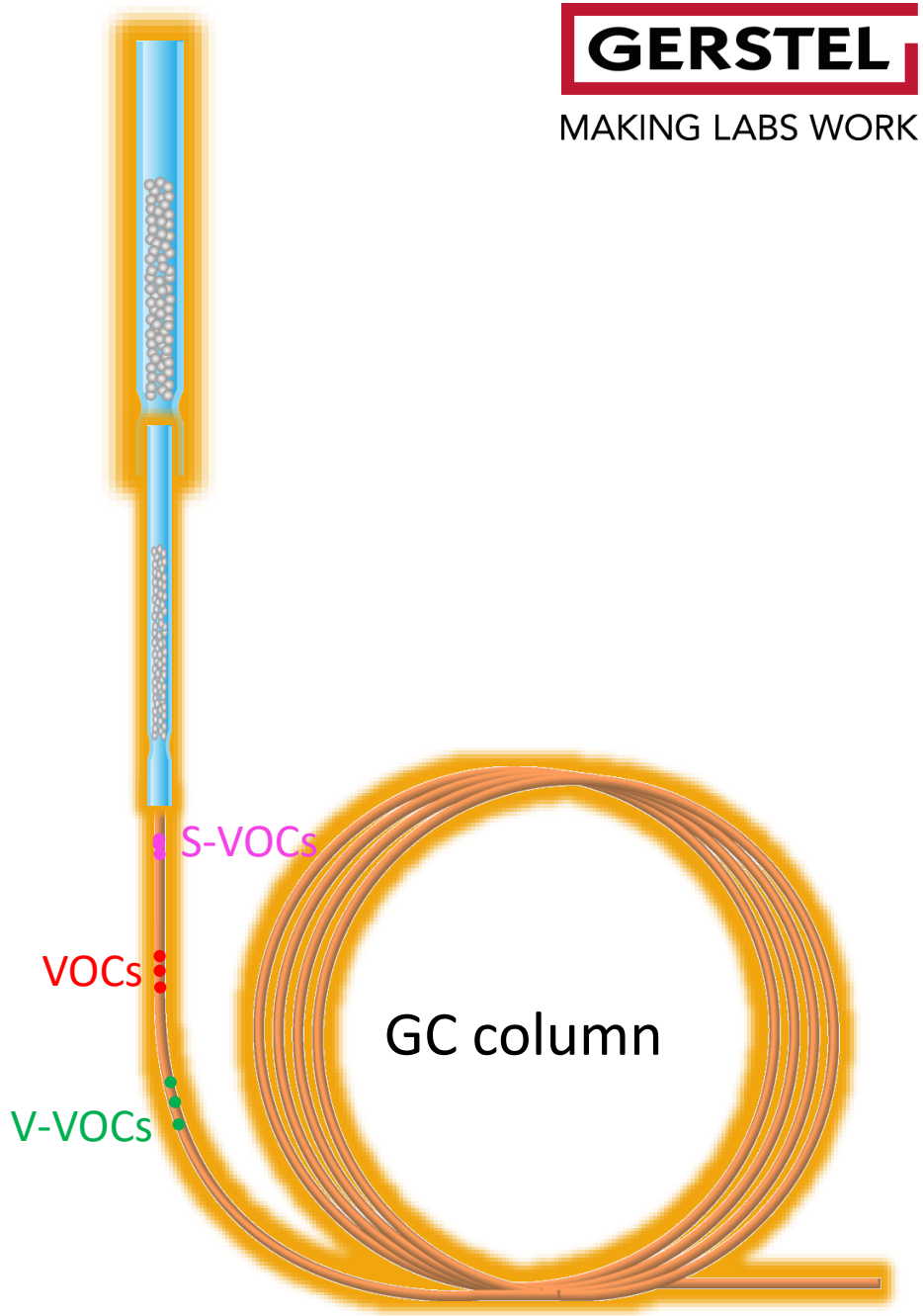
Static Focusing – GC Start





What are the Issues with Static Focusing?

- To statically focus VVOC's, like propylene and butadiene commonly seen in air methods, a very low trapping temperature is needed (usually done with liquid nitrogen)

- This is a great solution (particularly for non-targeted work) because "trapping with physics" is non-selective: chemical functionality doesn't matter, only boiling point

- However, cryofocusing requires regular attention to LN_2 supply, and reduces throughput due to LN_2 handling

What are the Issues with Static Focusing?

- Alternately, a multi-bed focusing trap (two, sometimes three sorbents) can be used to focus VVOC's a near-ambient temperatures, using Peltier cooling

- However, desorbing such a trap requires reversing the flow (backflushing) and this introduces 5-6 valves into the system and a transfer line

- That approach has complex plumbing and is prone to expensive valve replacement, reduced up-time due to complexity, and commonly carry-over of anything 'sticky'

What is needed did not exist up to now: a way to focus VVOC's without either backflushing a multi-bed trap and the required valves, or w/o trapping at low temps with either cryogens or other technologies. How can we have it both ways?

What is Dynamic Focusing?

- Instead of heating the TD tube to its maximum temperature quickly, a ramped heating program over several minutes is used
- While this is going on, the trap (with a single sorbent) is cooled but not enough to halt the analytes from moving – only to slow them down
- With pre-set timing and flows, the highest boiling species will be arriving at the focusing trap just as the lowest boiling species are ready to leave it

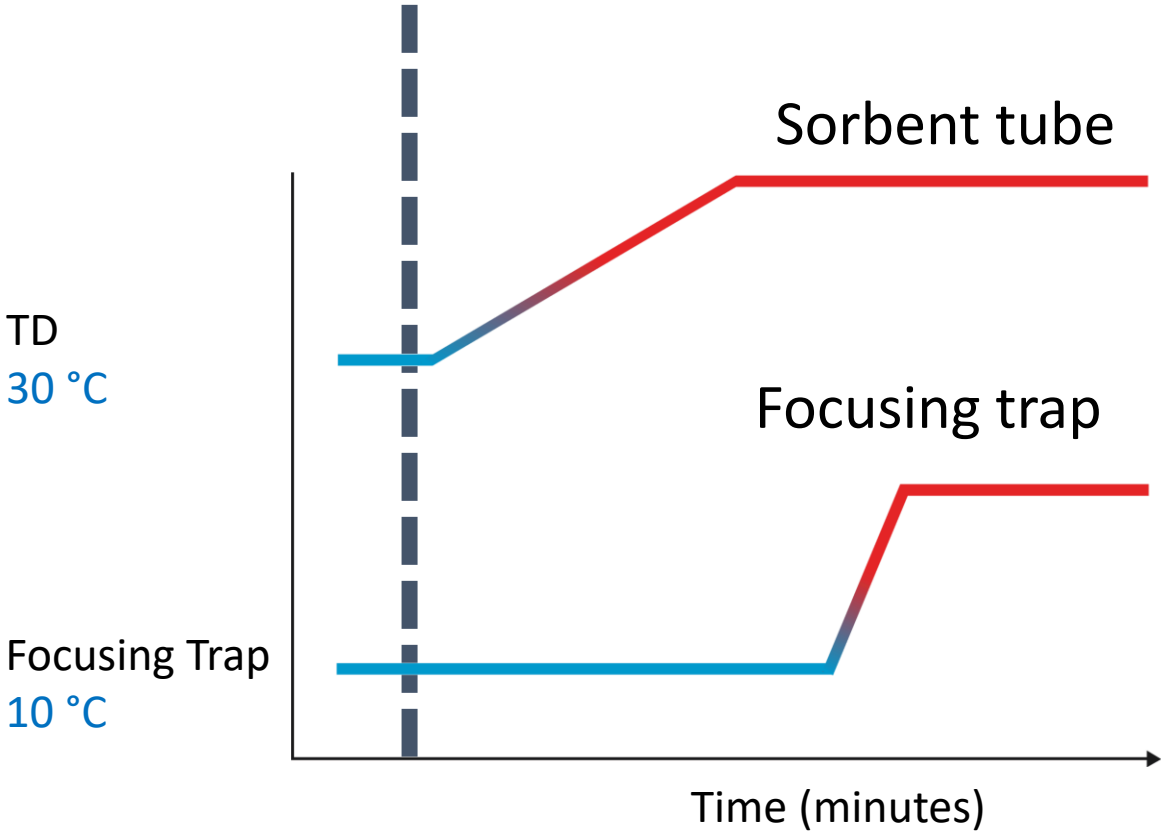
What is Dynamic Focusing?

- When all species are on the trap, it is rapidly heated and all analytes arrive at the column head together, for optimum chromatography

- Dynamic focusing is all about using a single sorbent (Tenax so far) and *proper timing* to analyze the full range of analytes in the method

Because Tenax is used (up to this point), and Tenax is hydrophobic, water management is greatly simplified. The temperatures used to trap analytes (+10 °C) are easily achieved using Peltier cooling (e.g., 'cryogen free').

Dynamic Focusing - Start



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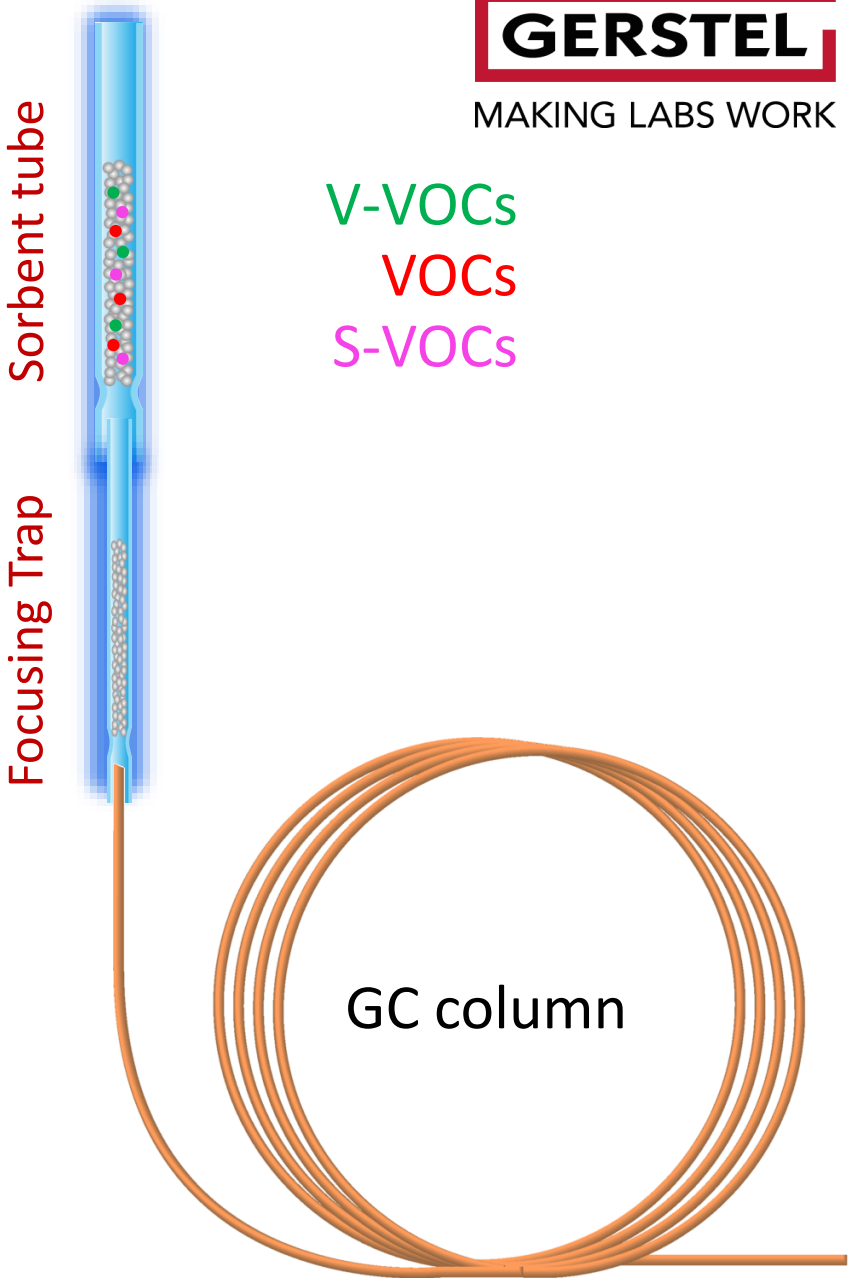
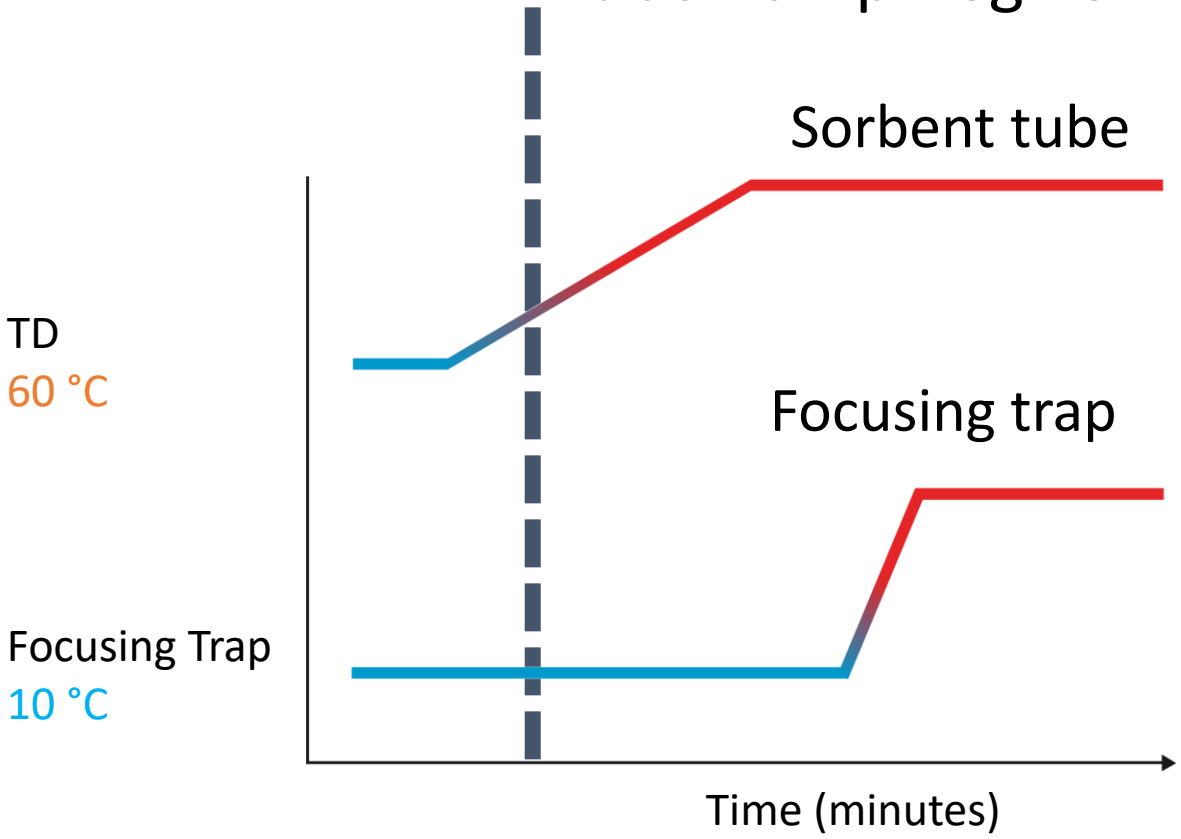
V-VOCs
VOCs
S-VOCs



Dynamic Focusing – Tube Ramp Begins



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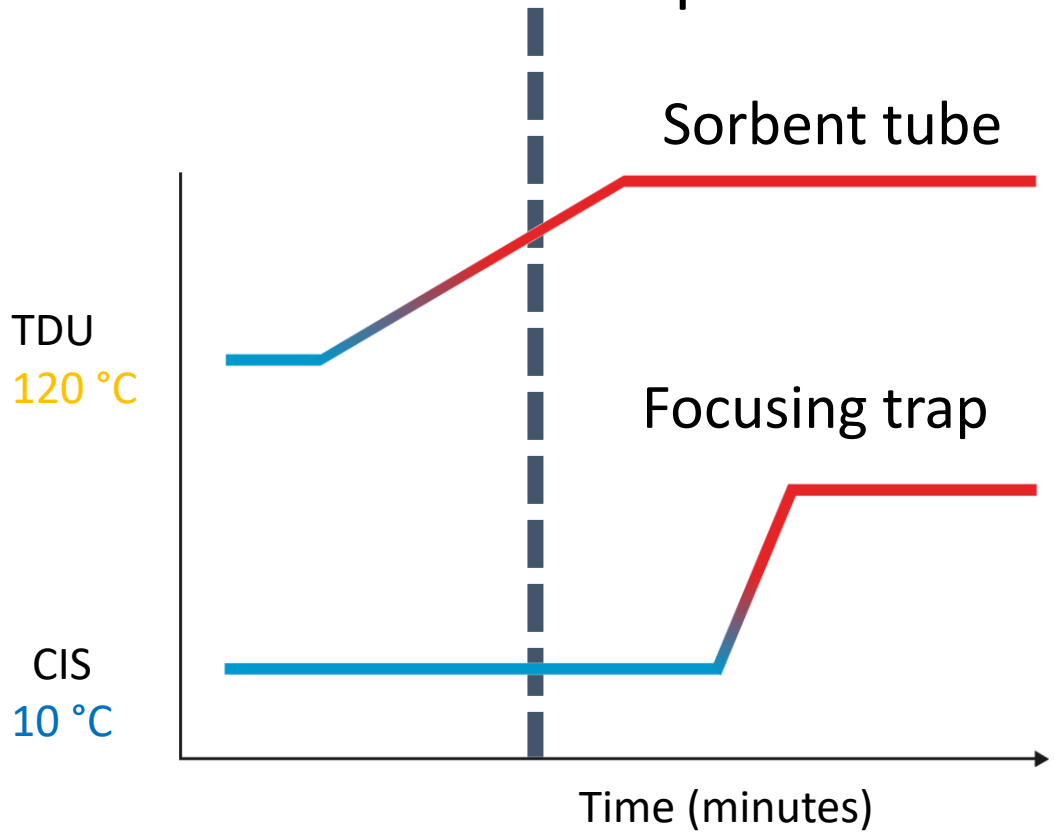
V-VOCs
VOCs
S-VOCs

Dynamic Focusing – Tube Ramp Continues



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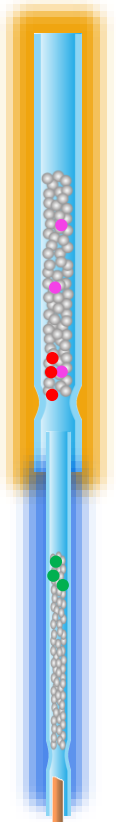
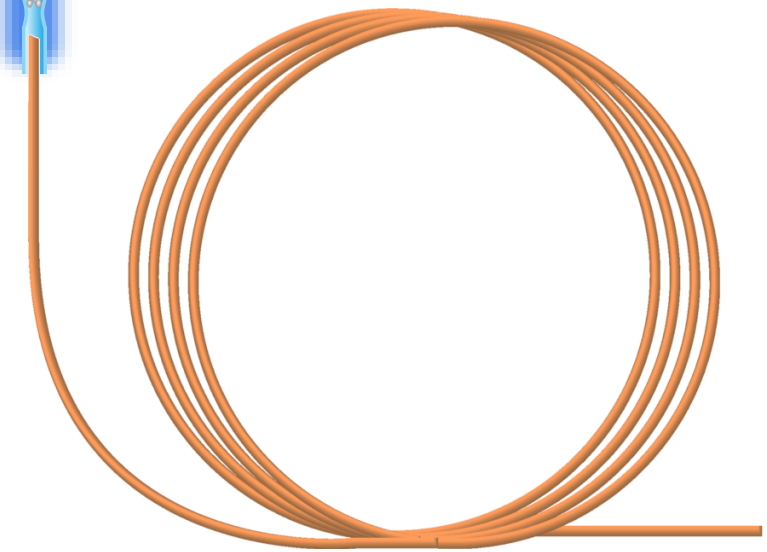


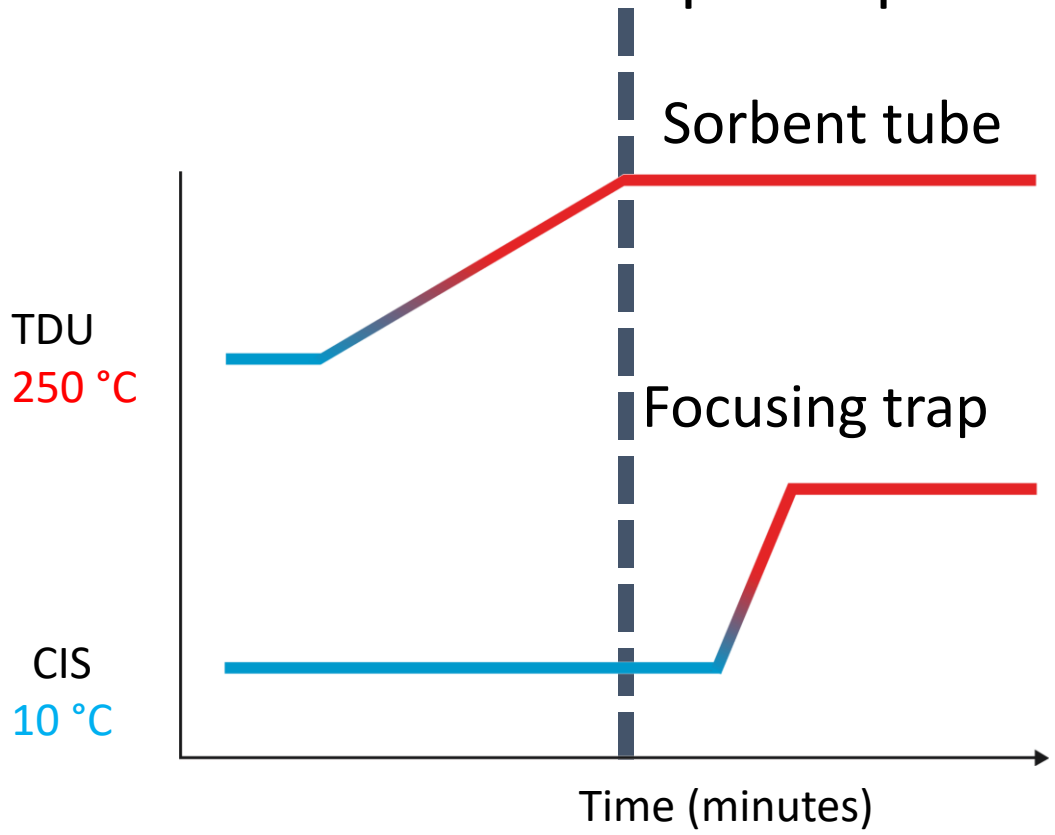
S-VOCs

VOCs

V-VOCs



Dynamic Focusing – Tube Ramp Complete



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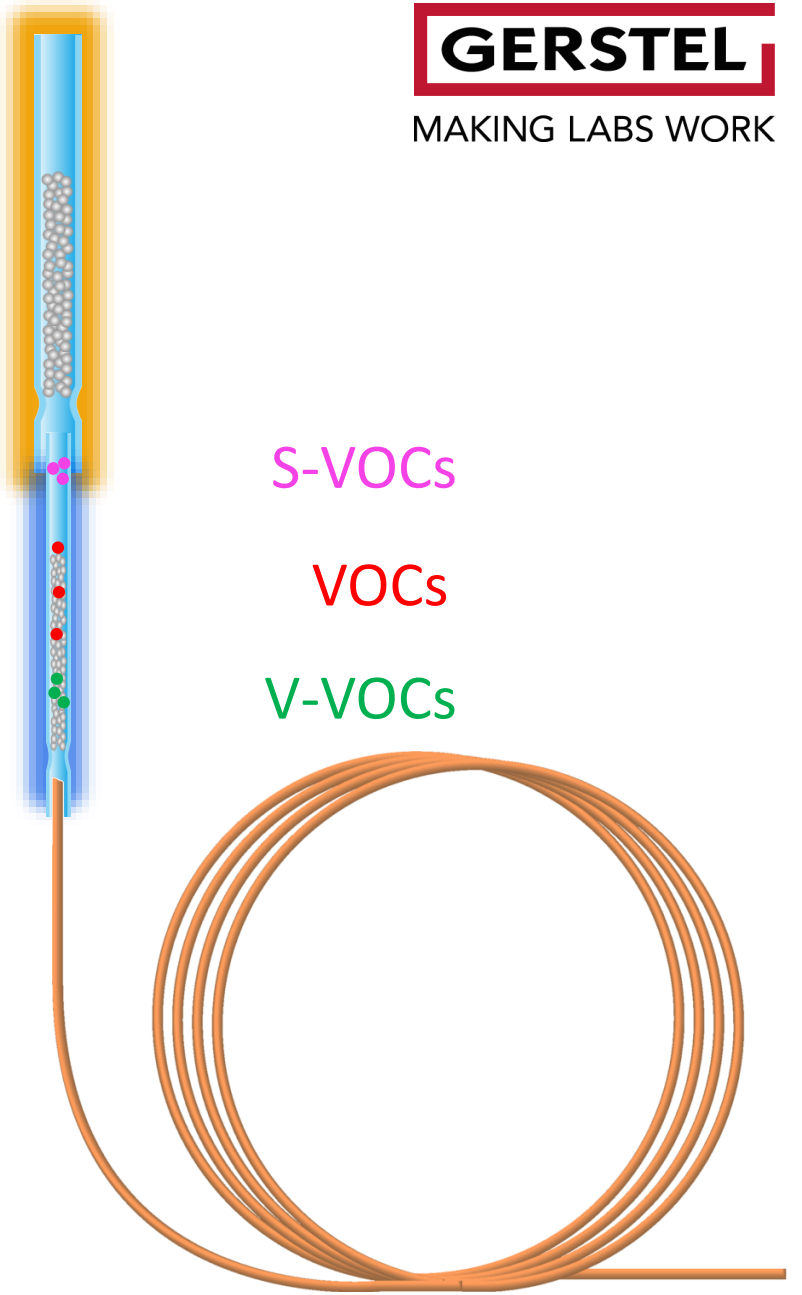
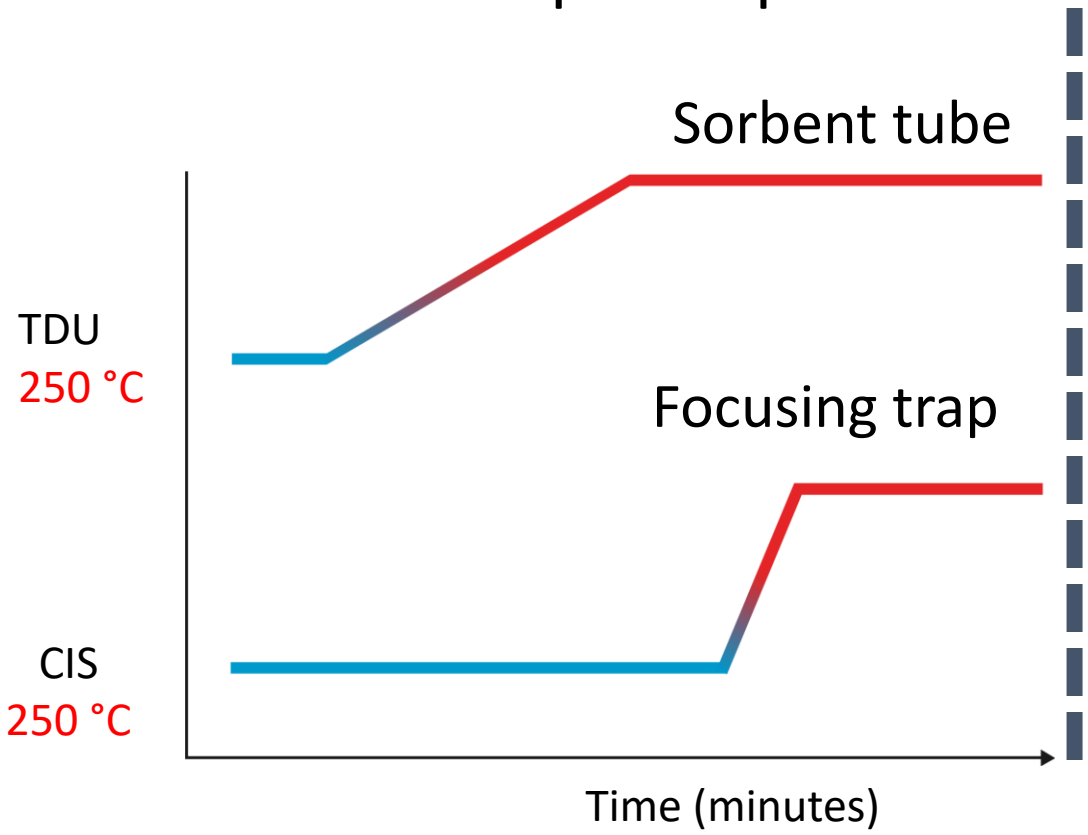
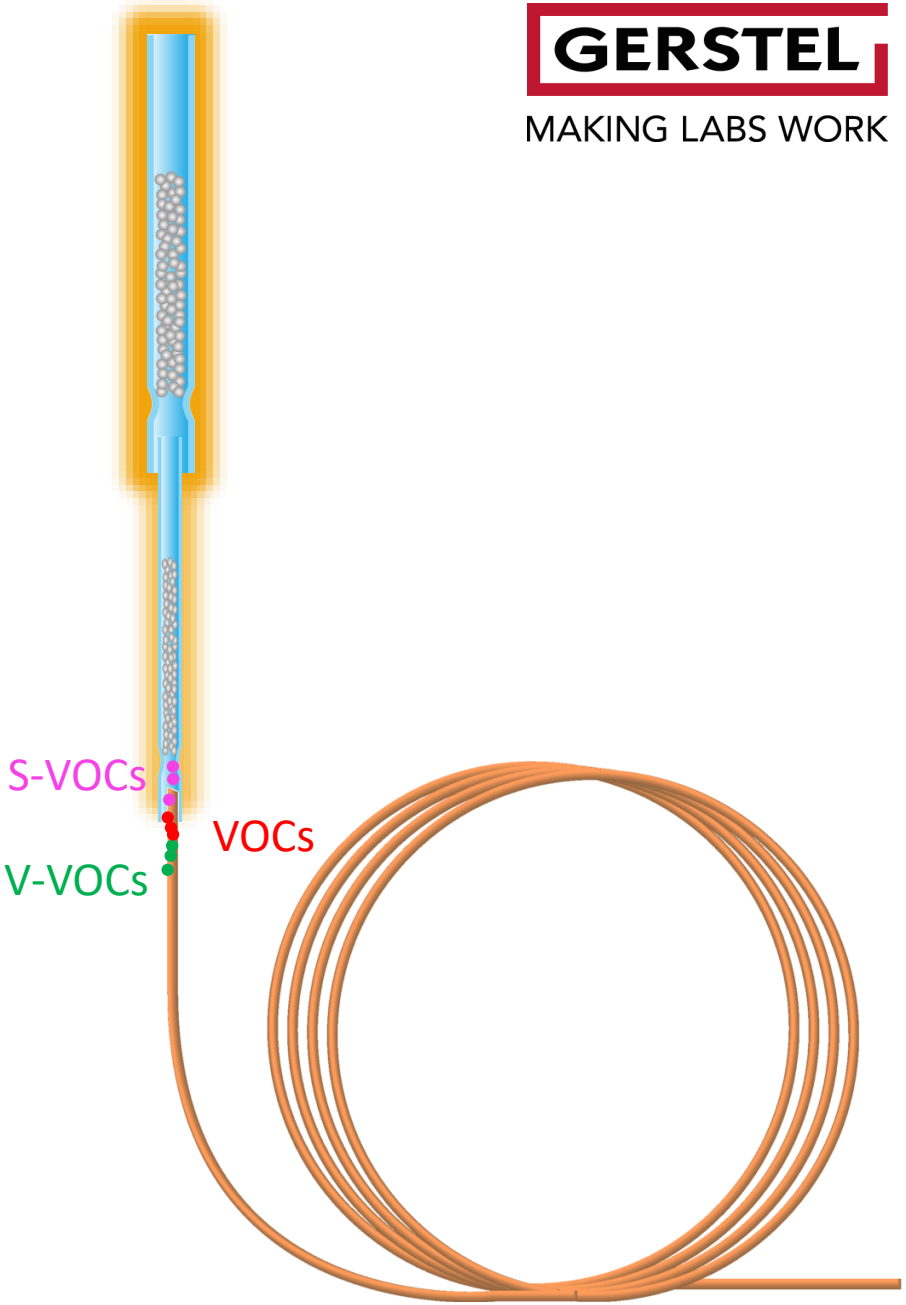


Dynamic Focusing – Rapid Trap Heat





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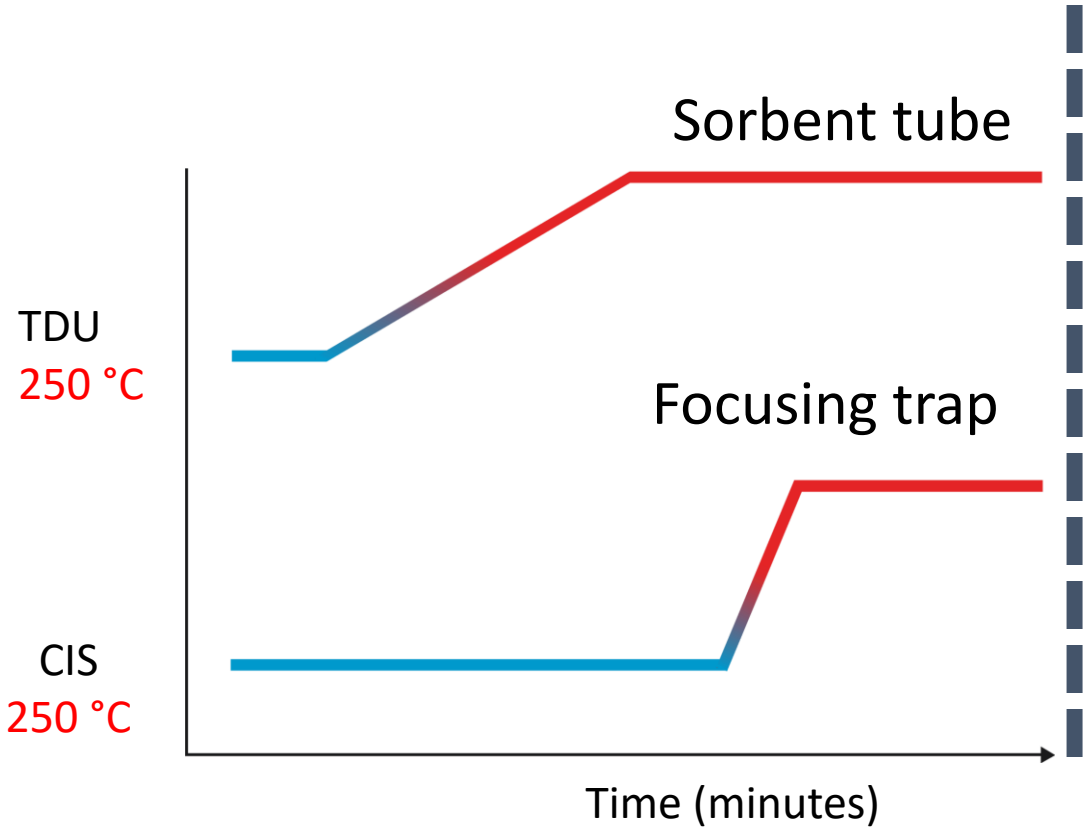
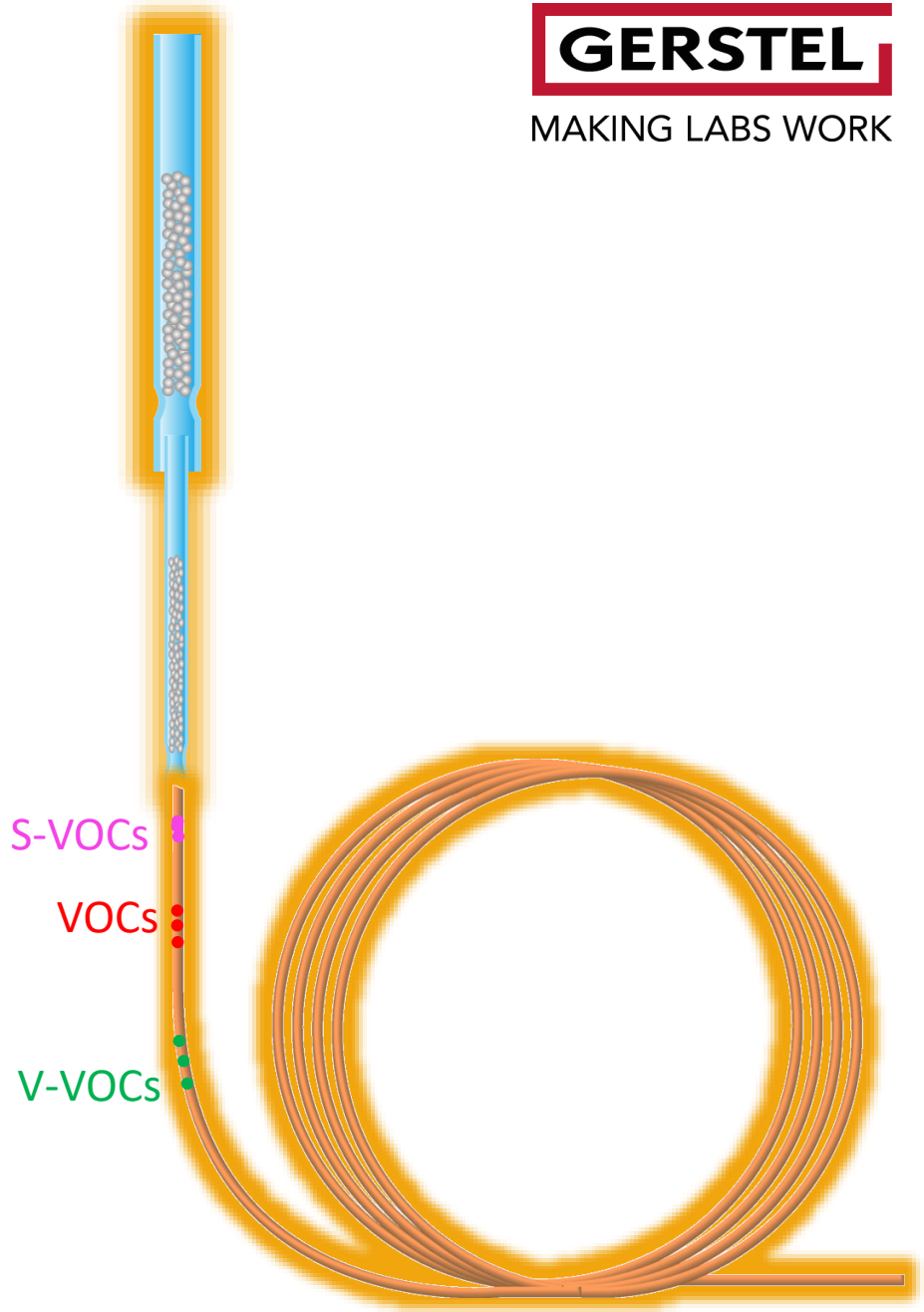
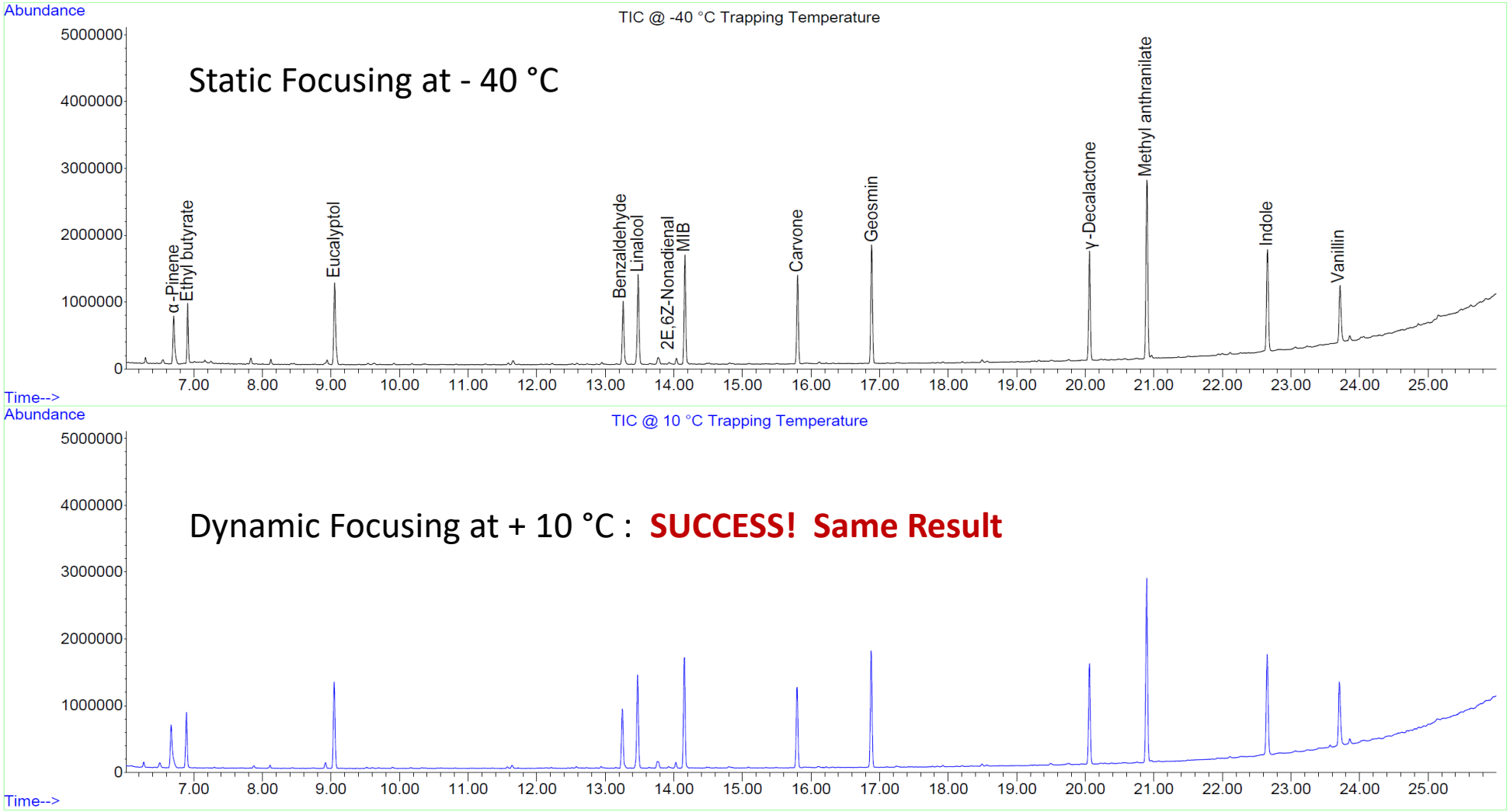
Dynamic Focusing – GC Start





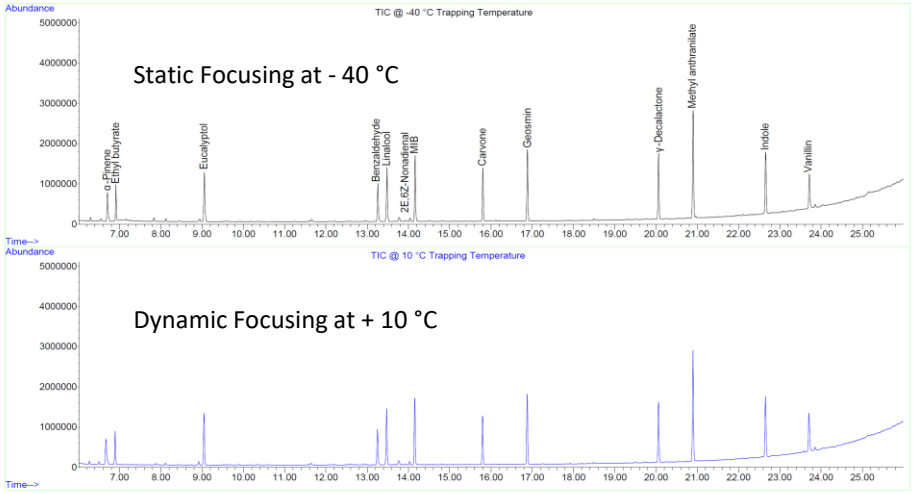
Mid-Boiling Odor Test Mix Standard



Stacked view of chromatograms obtained when the odor test mixture was trapped at -40 °C (top) and +10 °C (bottom).

Mid-Boilers = No Surprise

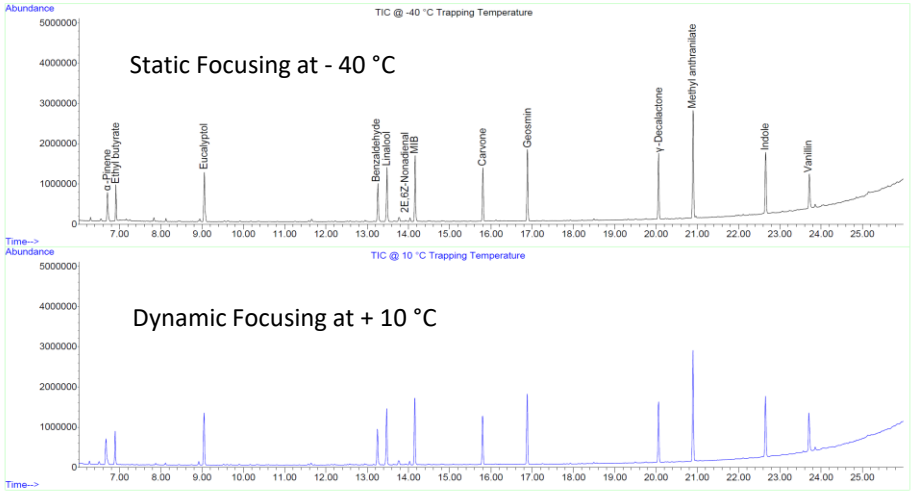
Mid-Boiling Odor Test Mix Standard



- After leaving the focusing trap, mid-boiling compounds will gather at the head of the column and refocus there
- In other words, even if Dynamic Focusing didn't work, it would have 'worked'
- Consequently, for mid-boiling compounds breakthrough at the focusing trap is irrelevant, even if it did happen
- However, note that the areas are the same in both cases and the retention times did not shift either
- This makes the case that breakthrough didn't occur at the higher (+10 °C) temperature and the Dynamic Focusing worked fine for these compounds

Mid-Boilers = Implications

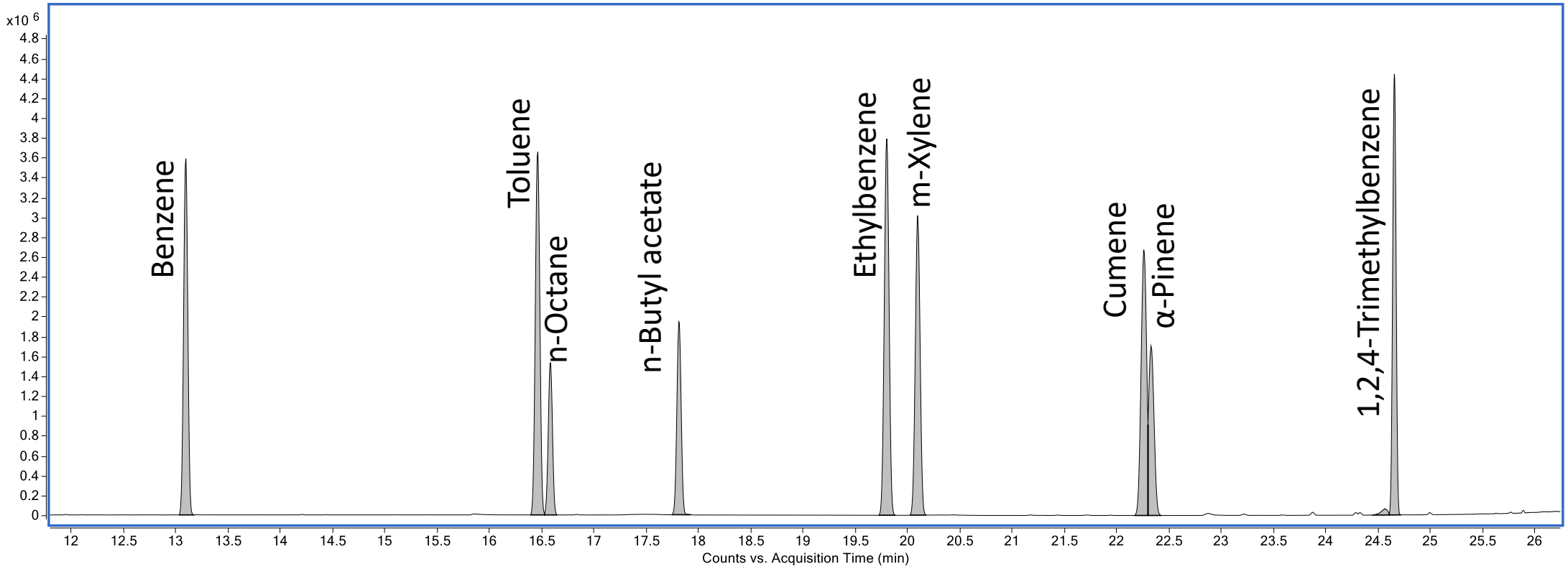
Mid-Boiling Odor Test Mix Standard



- Mid-boiling compounds are usually analyzed using TD tubes with Tenax TA in them, the same sorbent we are currently using for Dynamic Focusing
- Although we don't have extensive data to prove it in every case, so far anything trapped on Tenax TA works with Dynamic Focusing using a Tenax trap
- Tenax TA is the most widely used sorbent in the food/flavor/"brand protection" world, so DF will likely take hold there
- There is an additional world where Tenax TA filled sorbent tubes are commonly used….

ISO 16000-6 / ISO 16017-1 Indoor Air and Material Emissions Chamber Testing:

TD-GC-MS with Dynamic Focusing at +10 °C



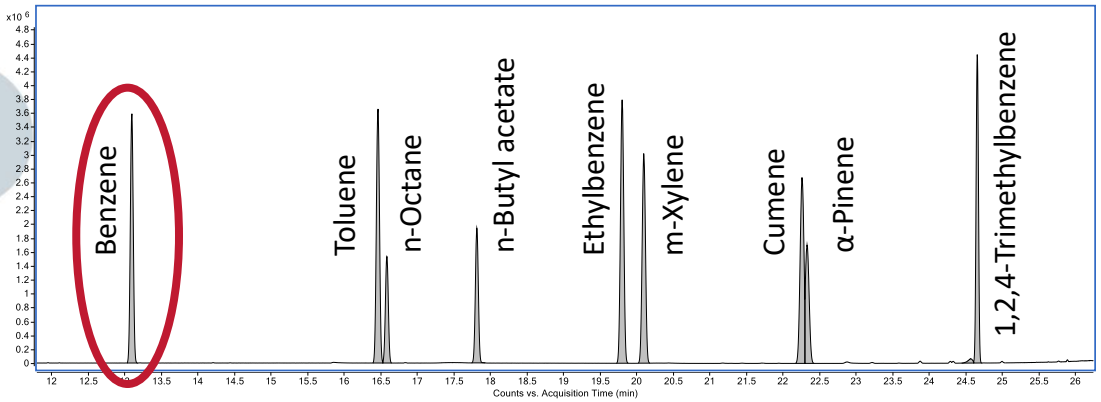
Indoor Air Round-Robin Test Chamber Sample

April 2023 Study by the German IfA (similar to OSHA in the US)

Dynamic Focusing and ISO 16000-6

Indoor Air Round-Robin Sample, April 2023

Study by the German IfA* (similar to OSHA in the US)



Analyte BP Range of DF at least as low as 80 °C

- The lowest boiling compound in this IfA Round Robin was Benzene, which shows good chromatography
- Benzene has a boiling point of 80 °C
- Thus Dynamic Focusing works for compounds with boiling points as low as 80 °C, to a first approximation
- Quantitatively, how did the Round Robin study come out?

*IfA = Institut für Arbeitsschutz

IfA Round Robin Test Results

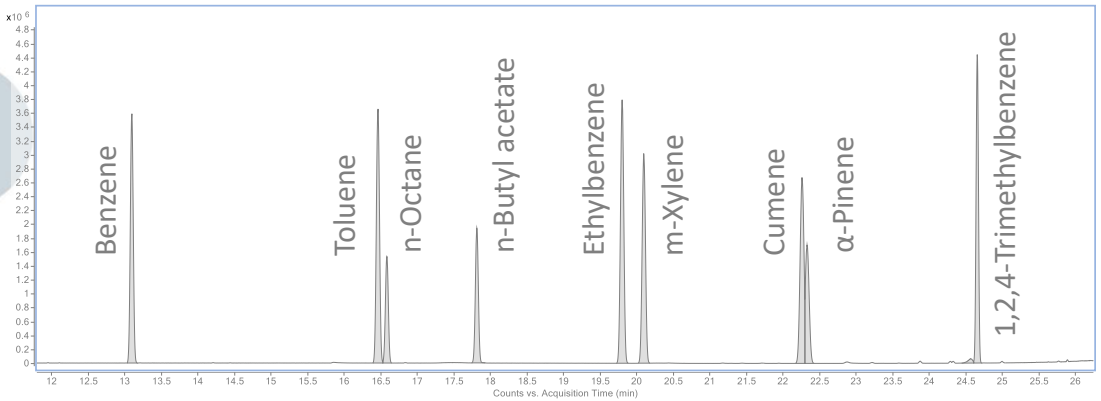
	Sample #1				Sample #2			
Analyte	Result [µg/m³]	Average [µg/m³]	Reference [µg/m³]	Outcome	Result [µg/m³]	Average [µg/m³]	Reference [µg/m³]	Outcome
1,2,4-Trimethylbenzene	43.1	50.4	54.9		30.9	26.3	31.1	
α-Pinene	69	86.8	87.2		67.3	69	67.5	
Benzene	21.4	24.8	28.3		62.7	59	61.3	
Cumene	36.1	33.7	36.8		43.7	33.8	36.1	
Ethylbenzene	61.9	70.4	72.9		44.2	43.3	45.4	
m-Xlyene	105	136	132.4		89.3	90.3	87.7	
n-Butyl acetate	32.7	37.6	42.2		126	138	140.1	
n-Octane	55.9	66	67.1		121	132	131.8	
Toluene	82	101	102.7		53.8	50.8	51.7	

- Two samples were taken from two IfA test chambers (two concentrations), and at 20 °C and 35% RH
- Tenax TA tubes were used; sampling volume was 2 Liters (66 mL/min for 30 minutes)
- Although the tubes could have been dry purged before analysis, they were not (Tenax is 'hydrophobic')
- Dynamic Focusing was used for this work; the lab successfully passed this Round Robin, validating the success of Dynamic focusing in standard methods

Dynamic Focusing Successful for Indoor Air Methods, Including Similar Industrial Hygiene Methods

Indoor Air Round-Robin Sample, April 2023

Study by the German IfA* (similar to OSHA in the US)



Analyte BP Range of DF at least as low as 80 °C

- The lowest boiling compound in this IfA Round Robin was Benzene, which has a boiling point of 80 °C
- How “low can we go” in terms of analyte boiling points?
- Or, does Dynamic Focusing work for ‘VVOC’s’?
- Water was also not much of an issue in that Round Robin (only 35% RH); how should we test the performance of a ‘wet sample’?

So What Next?

US EPA Method TO-17 “Air Toxics”

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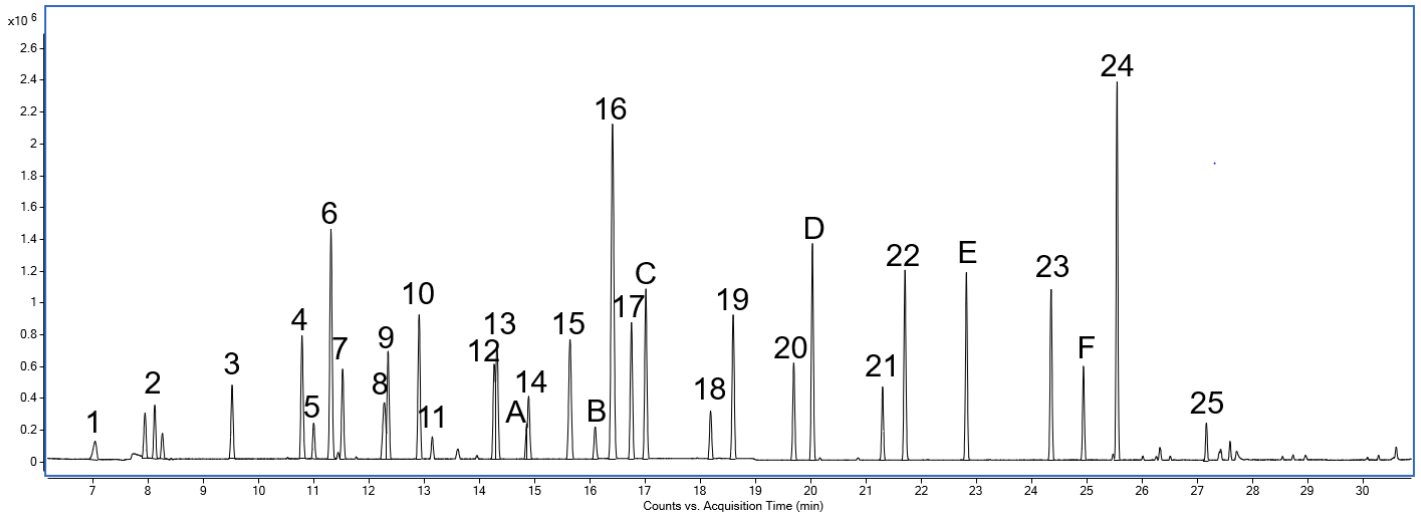
- TO-17 covers a range from propylene to naphthalene (or higher; GC column dependent)
- In terms of boiling point, that’s -48 °C to +218 °C
- Wide range of classes: hydrocarbons, aromatics, halogenated hydrocarbons, and aldehydes / ketones
- This will require the sampling tube to have multiple sorbents, including typically molecular sieves
- Detection limits are 0.5 ppb V/V using an MSD in scan mode (SIM would be lower) and a ‘624’ type column
- Sample precision of 20% RSD or better; calibration via Relative Response Factors (RRF), precision of ≤ 30%
- Water management: TO-17 is an ‘ambient air method’, so humidity values ranging from what you’d find in Barrow Alaska in January to Houston Texas in August
- Consequently, and taking the molecular sieves in mind, dry purging to remove captured water before analysis is required
- Although not strictly required, in real-world examples gas-phase internal standards are used to compensate for instrument drift; TD tubes are automatically spiked with ISTD gas immediately before analysis

TO-17 Calibration Mix
Neat standard



Analytes					
1	Propylene	10	n-Hexane	19	Bromodichloromethane
2	1,3-Butadiene	11	Vinyl acetate	20	Methyl isobutyl ketone (MIBK)
3	Vinyl Bromide	12	Butanone (MEK)	21	2-Hexanone (MBK)
4	Acetone	13	Ethyl acetate	22	Dibromochloromethane
5	2-Propanol	14	Tetrahydrofuran (THF)	23	Bromoform
6	Carbon disulfide	15	Cyclohexane	24	4-Ethyltoluene
7	Allyl chloride	16	iso-Octane	25	Benzyl chloride
8	Methyl tert-butyl ether (MTBE)	17	n-Heptane		
9	Dichlorethene	18	1,4-Dioxane		
Internal Standards					
A	Bromochloromethane	C	Difluorobenzene	E	Chlorbenzene-d5
B	Dichloroethane-d4	D	Toluene-d8	F	1-Bromo-4-fluorobenzene

- Good chromatography overall; Dynamic Focusing “works” for analytes as small as propylene!
- All internal standards introduced as a 1.00 mL spike of gas onto the TD tube before analysis, using an “ISDP Station” on the A/S
- Samples were taken using Air Toxics tubes, 50 mL/min for 20 min (1 L sample)
- Overall 10:1 split, 624 column (35°C hold for 3.5 min, Ramp 1 10°C/min to 240°C, Ramp 2 30°C/min to 300°C hold for 5 min)
- MSD in scan mode, 33-300 m/z

TO-17 Calibration Mix
Selected Calibration Data

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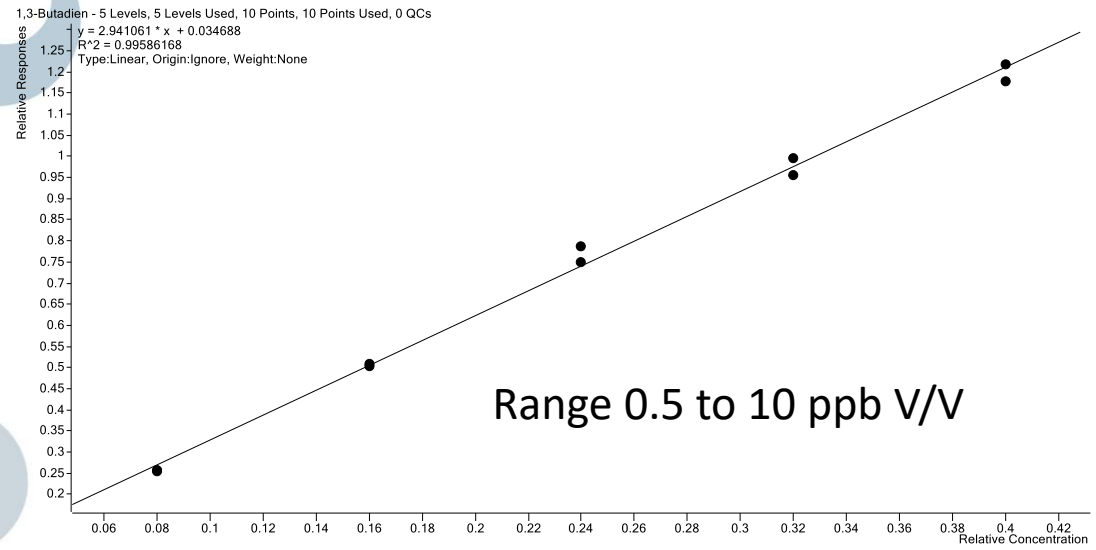
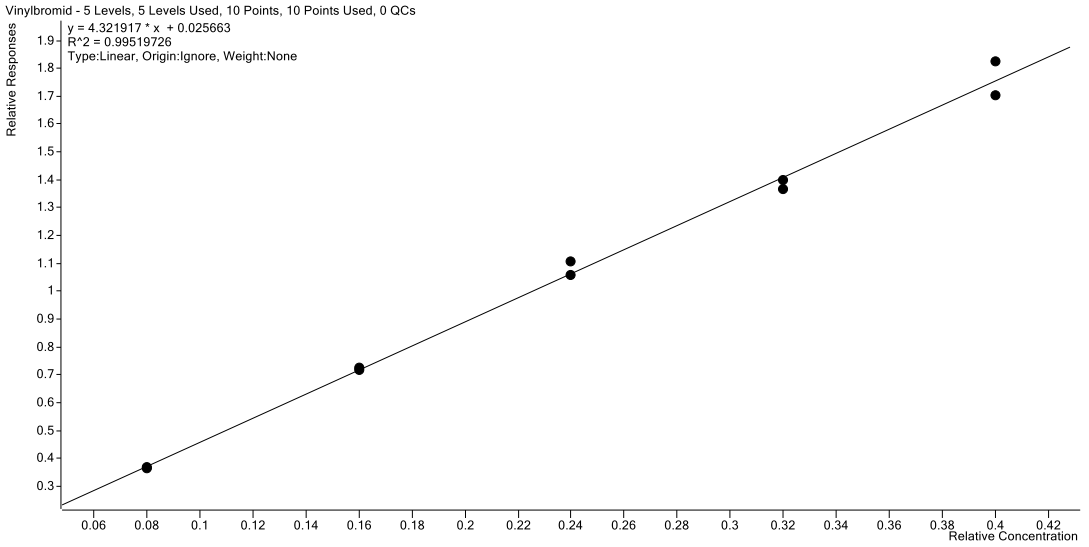
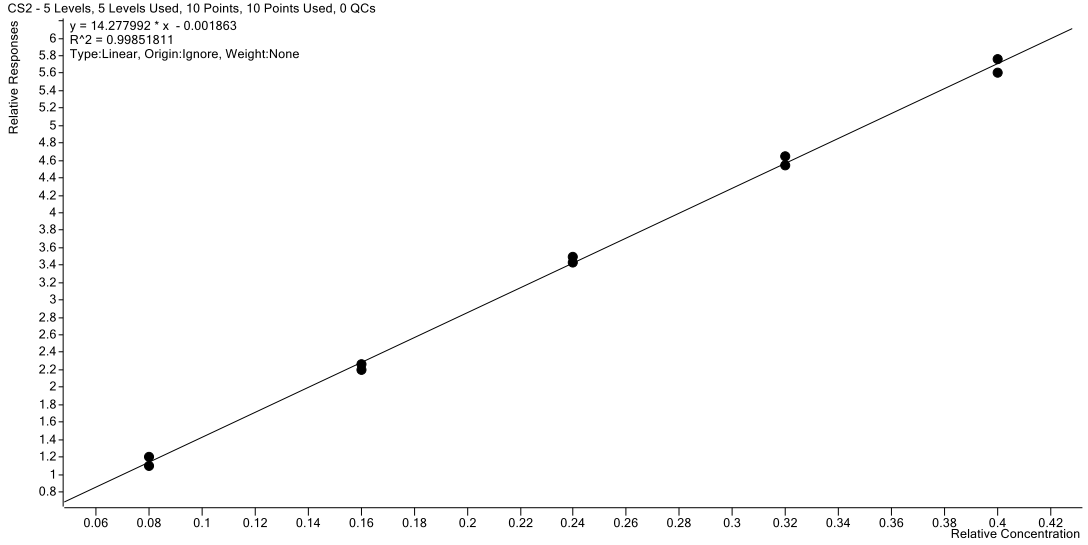
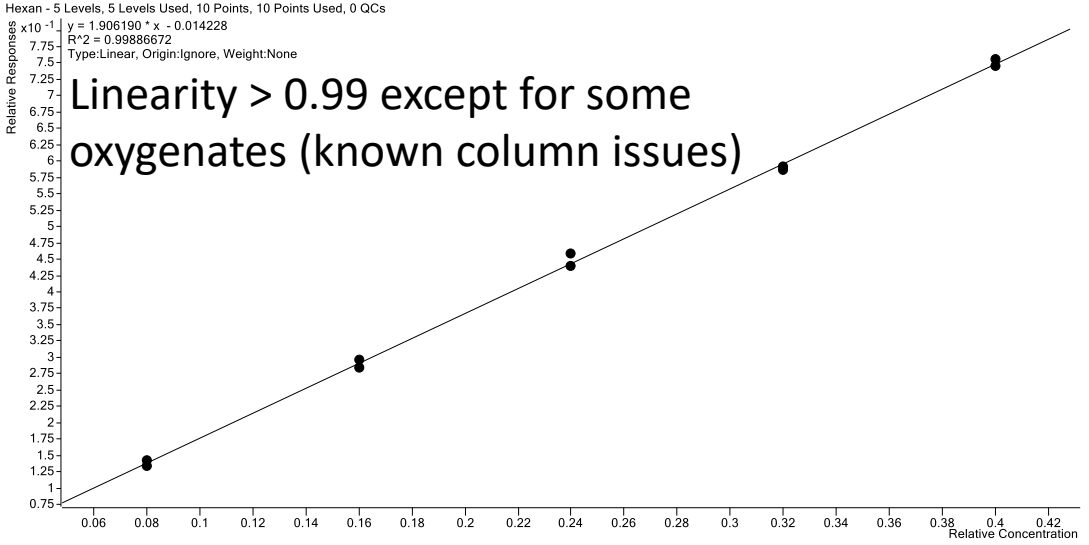


Range 0.5 to 10 ppb V/V







Linearity > 0.99 except for some oxygenates (known column issues)

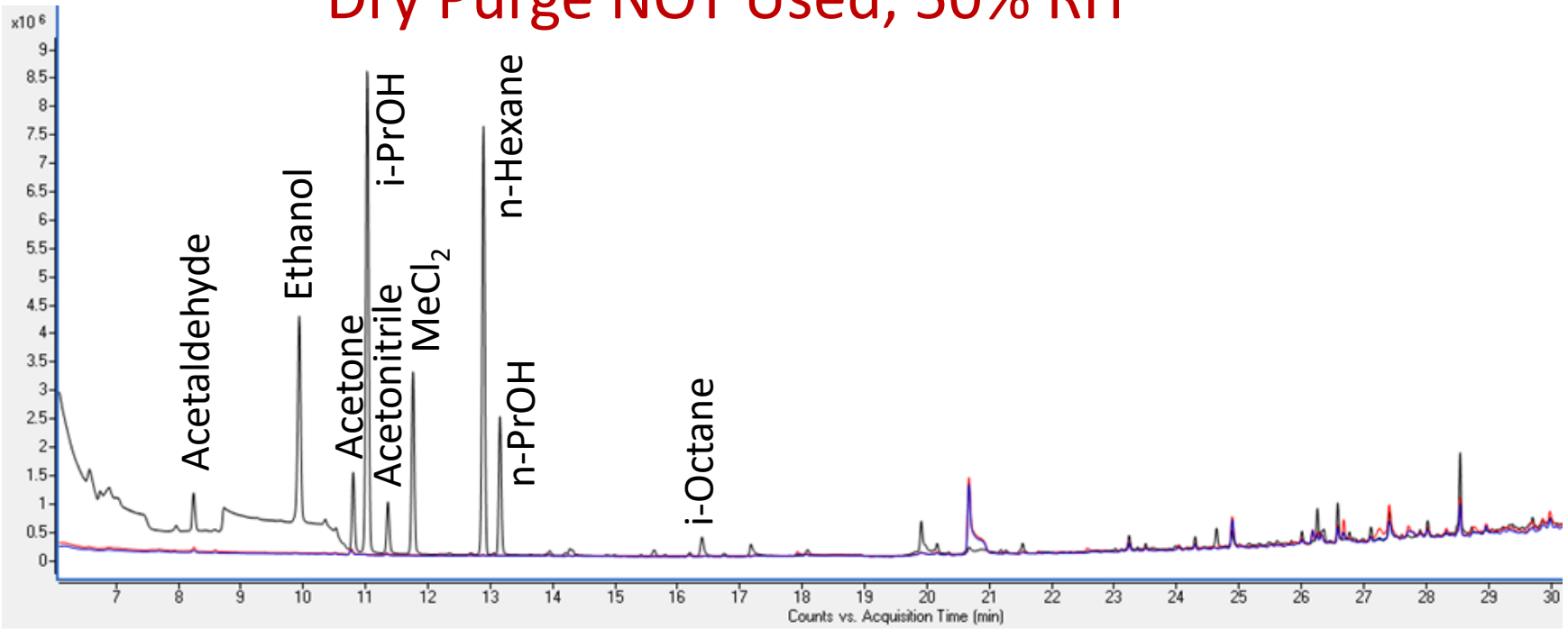
VVOC Portion: D/L, Precision, Linearity

Analyte	S/N	Precision = RSD [%, n=3]			Relative Response Factors	
	0.5 ppb	0.5 ppb	3 ppb	6 ppb	absolute	RSD [%]
Propylene	12.4	14.1	6.2	7.5	0.09	12.5
1,3-Butadiene	30.6	3.0	3.3	1.8	0.37	16.9
Vinyl bromide	70.1	3.4	2.2	5.6	0.52	16.4
Acetone	194.3	10.6	16.3	13.0	0.60	8.2
Isopropanol	121.3	31.2	18.3	4.8	0.02	18.9
Carbon disulfide	515.2	13.9	1.8	4.6	2.11	18.3
Allyl chloride	5.4	10.5	1.1	4.5	0.09	23.3
MtBE	14.9	6.7	5.6	2.3	0.60	10.8
Dichlorethylene	29.2	5.9	1.2	0.3	0.11	24.5
n-Hexane	69.5	15.4	6.3	0.3	0.27	20.6

- As mentioned previously, the challenge for Dynamic Focusing is at the light end, not the mid or heavy ends
- Chromatography was already successful; this data shows that DF is successful quantitatively for VVOC's as well
- Precision is 20% or better, D/L's are ≤ 5 ppb V/V and likely 10x below that in most cases (via 40 CFR 136 method)
- D/L's could be further improved by lowering the split, going to SIM/Scan mode, or other detector-related items
- System using DF is in place at the German BAM and is meeting all analysis QC and requirements; will Round Robin soon

“Real” Air Sample: Lab Air, 250 mL

Dry Purge NOT Used, 50% RH



- Nearly all are solvents (used in the LC lab nearby) and in the low ppb range
- The blue and red traces are blanks placed from the autosampler for several hours (blue) then re-ran (red)
- Despite the ambient contamination of the lab air, the blanks were not contaminated by it at all
- Carbon Dioxide can still be seen in baseline up to about 11 minutes (typical for TO-17 when mol sieves are used)
- Most of the remaining peaks are column bleed; see upcoming application note for full descriptions

Dynamic Focusing: What Does it Mean?

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- Trapping with Dynamic Focusing can determine most compounds at +10 °C using a single sorbent for focusing/trapping, and covering the ‘full range’ of compounds (‘full range’ is GC column dependent)
- Dynamic Focusing does not require valves, filters and transfer lines used in backflushed architecture and eliminates the problems associated with their use, like analyte loss, carry-over, and maintenance
- Since a single sorbent is required for Dynamic Focusing, the issue of bleed or degradation over time causing artifacts or poor analytical performance is present (although less), but this is true for any system that focuses and traps using sorbents (traps using ‘chemistry’).
- **Take Away Message:** If you know what you are looking for (target analysis) and have standards that you can run to ensure system performance, you can confidently use Dynamic Focusing to get the **full range** of compounds, but without cryogenic cooling **and without a valve and transfer line**.
- For vapor intrusion and other ‘hot’ samples, dynamic focusing without valves & transfer lines will greatly reduce clean-up runs after “hot samples” and extend the use of TD-GC-MS further

Dynamic Focusing – When Can it be Used

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1. For targeted analysis where some means of making sure the draw backs of using sorbents in the trap (bleed, artifacts, compound loss & carryover) are not affecting the analysis.
2. When samples are collected using Tenax TA tubes, Dynamic Focusing can almost always be used with little method development.
3. When samples are collected using other sorbent tubes, Dynamic Focusing can almost always be used but will require method development and validation.
4. If water is still an issue after dry purging, Dynamic Focusing with Tenax has no molecular sieves, so any remaining water is not as likely to be retained; DF is the best option for humid samples
5. Direct thermal desorption with short tube desorption times when light compounds (below hexane) are not of interest (such as VDA278, a vehicle indoor air quality method).

Dynamic Focusing – When it Shouldn't be Used

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1. For non-targeted analysis (true unknowns). Only non-selective, 'comprehensive' focusing and trapping using a glass bead packed liner at -120 °C ('trapping with physics') should be used instead
2. Analyses that are very sensitive to Tenax bleed and degradation artifacts (benzene, benzaldehyde, or α-methyl styrene) (unless/until a different sorbent is used for Dynamic Focusing)
3. Determination of high boiling compounds (PAHs) and high boiling matrices, but those kinds of compounds are easily done "normally" with glass beads and a DB-5HT or similar.
4. Oddly, C4-C8 PFAS Acids (but FTOH's, FTAC's, etc. all do fine). Interesting research topic…
5. True splitless/splitless desorption – Dynamic Focusing requires a split during tube desorption; SL/SL analysis is typically not recommended anyway, for other reasons, and recollection is not possible in splitless mode.

DF is still evolving; sorbents, parameters, and trap geometry are all topics of active research

Conclusions

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- “Backflush the trap with multiple sorbents” has been gospel for TD-GC-MS since the mid 1980’s. We have discovered that equivalent results can be done using a single sorbent, in a ‘straight through’ architecture
- For indoor air or ambient air, dynamic focusing produces the same results and passes method validation regimes
- Figures of merit, which are based mostly on the GC and MS used, are the same
- However, the simplified design used in DF (tube to trap, trap to column, no plumbing in between) will result in less carryover, compound loss, reduced downtime, and overall upkeep costs
- Water, either using a dry purge station or not, is easier to manage without a molecular sieve in the focusing trap
- **Take Away Message: Focusing “Air Toxics” compounds, esp. the VVOC portion, was not supposed to work on a single relatively weak sorbent bed, but it does, and it has a lot of advantages for the analyst and laboratory overall**

Our Gratitude

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Questions?