DHS as flexible Sampling Tool for Chemical Analysis

5th SBSE International Meeting 2019

23rd of September, Paris

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5TH SBSE INTERNATIONAL MEETING
23 & 24 SEPTEMBRE 2019 - NOVOTEL PARIS-SUD

SBSE Technical Meeting

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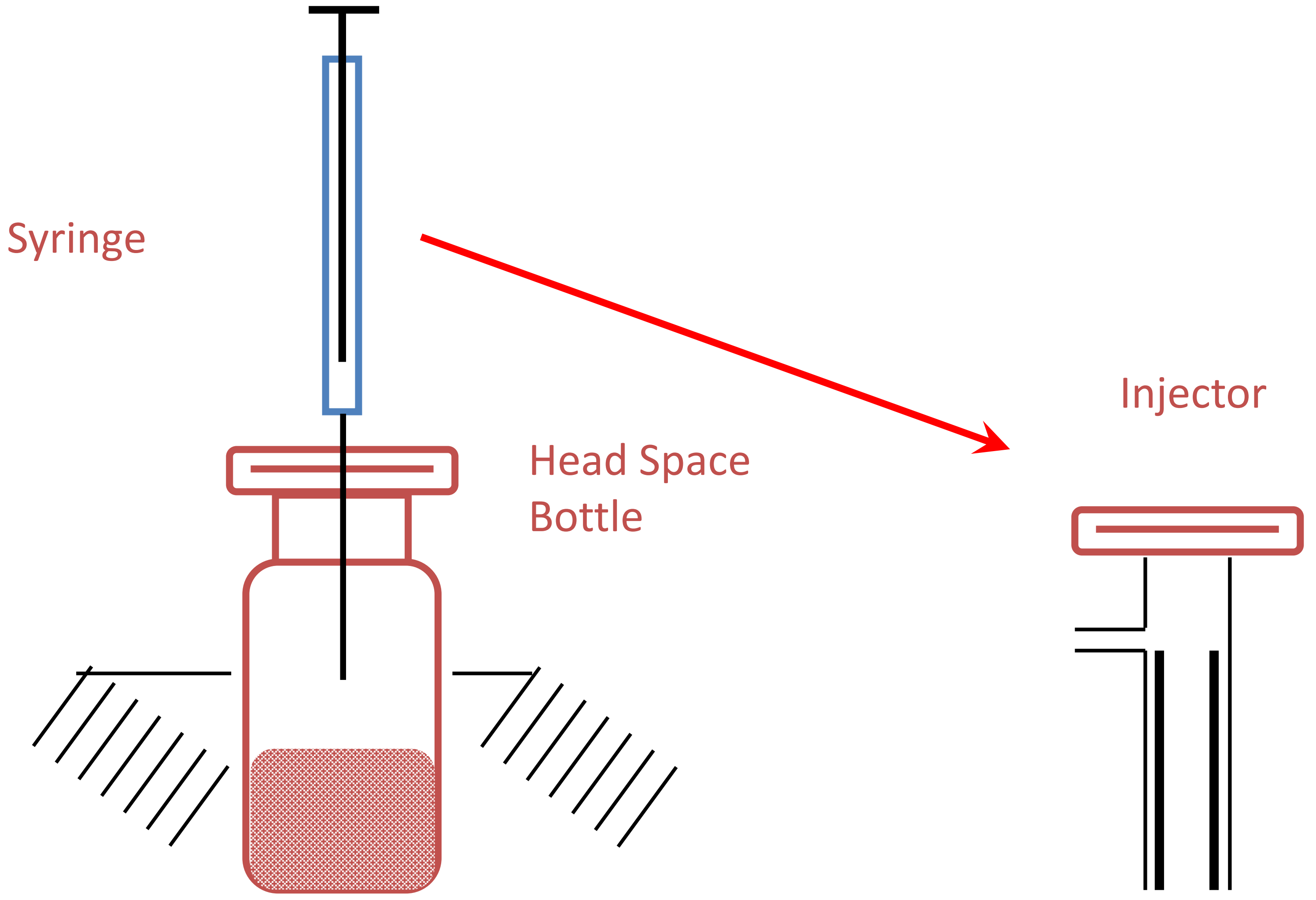
30 YEARS OF EXCELLENCE

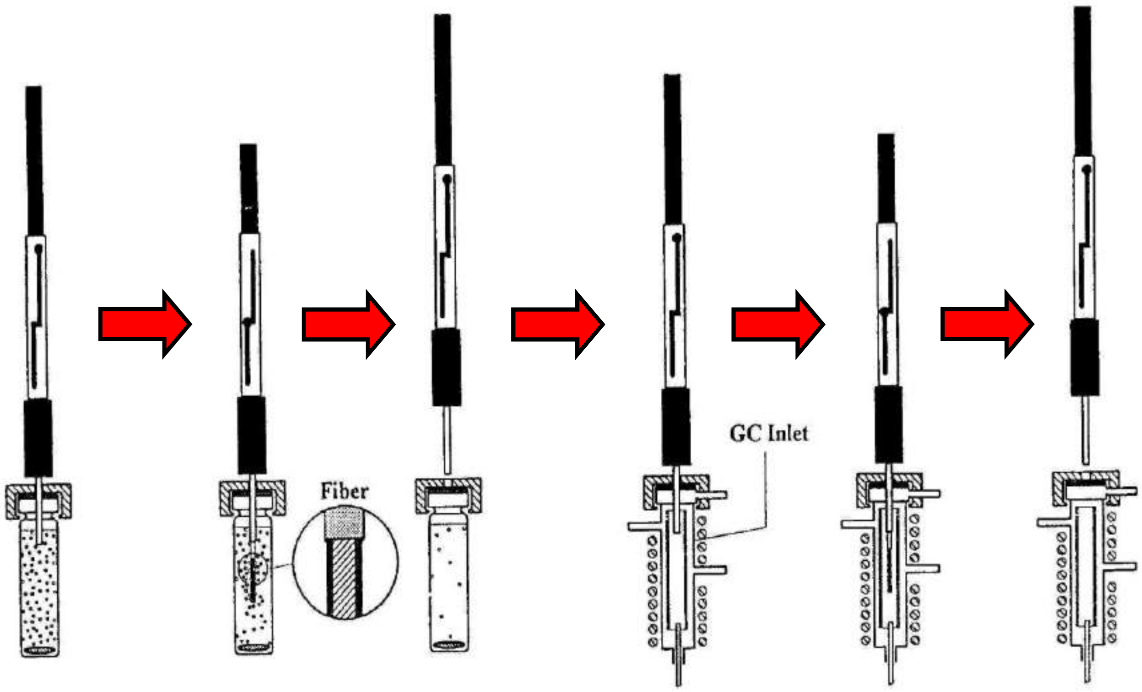
Sample Preparation Methods for Volatiles

- **Static Headspace (SHS)**
  - Single equilibrium + single injection = classical SHS
    - CTS-2 refocusing
  - Multiple headspace extraction (MHE)
    - Multiple runs (= Kolb method, e.g. Monomers in polymers)
    - Multiple sampling + single run (eg HIT-SHS, ITEX)
- **Dynamic Headspace (DHS)**
  - CTS-2 refocusing
  - Purge & Trap (P&T)
- **Sorptive Extraction**
  - **Solid Phase Micro-Extraction (SPME)**
    - New: SPME Arrow (increased volume of extraction phase)
  - **Stir Bar Sorptive Extraction (SBSE)**

Static Headspace (SHS)



Solid Phase Micro-Extraction (SPME)



Pierce sample septum — *Expose fiber Extract* — *Retract fiber Remove*

SORPTION

Pierce GC Inlet septum — *Expose fiber Desorb* — *Retract fiber Remove*

DESORPTION

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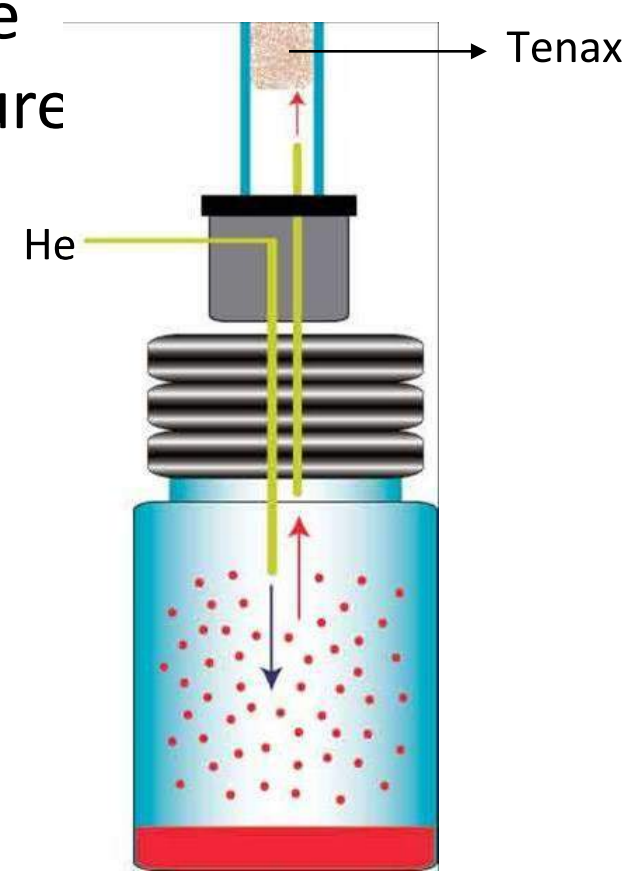
Dynamic Headspace (DHS)

- Continuous purging of headspace (sample) at controlled temperature for controlled time at controlled flow.
- Trapping of VOCs (adsorbent, sorbent, 20 °C – 70 °C)
- Thermal desorption of trap
- Goal: “exhaustive” extraction = highest sensitivity



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Importance of DHS in Chemical Analysis

- Importance in Flavor analysis – Perception:

"no technique can deliver the same results as steam destillation (or SAFE)"

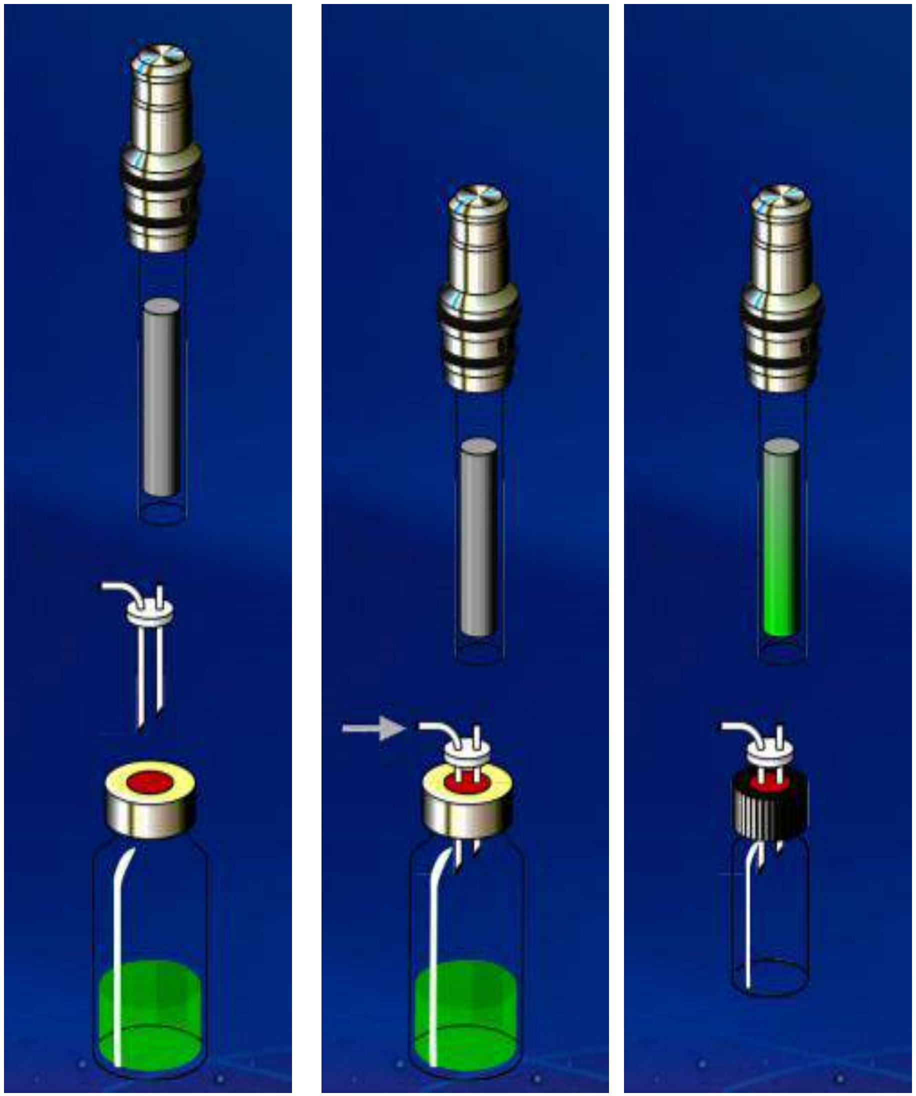
- Only LLE can deliver full chromatographic profiles covering a wide enough volatility range

- DHS versus Purge & Trap: Sensitivity within the analysis of volatiles

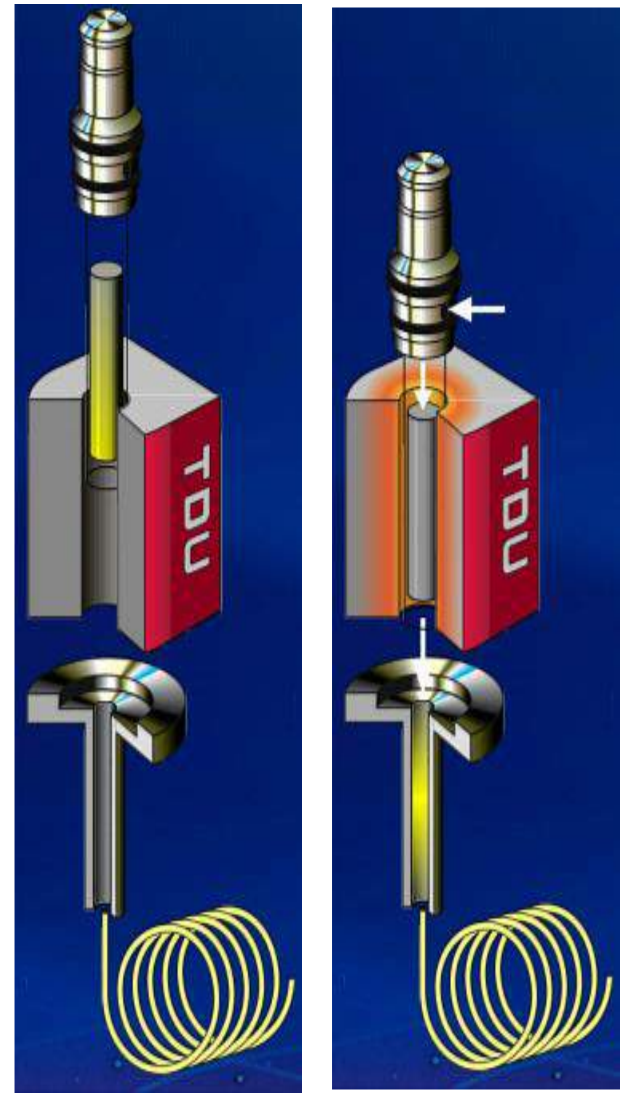
Gerstel DHS:

- **Sensitivity (exhaustive extraction ?)**
- **Fully Automated - Final step in sample prep automation**
- **Reduced cross-contamination (e.g. compared to P&T)**
- **Flexibility (different modes): DHS > FEDHS > MVM > DHS/CTS-2 > SE-DHS**
- **Probably the closest to SDSE & SAFE: "full" profile**

DHS



TDU



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TDU/PTV combination

Liquid injection of extract directly into a TDU insert

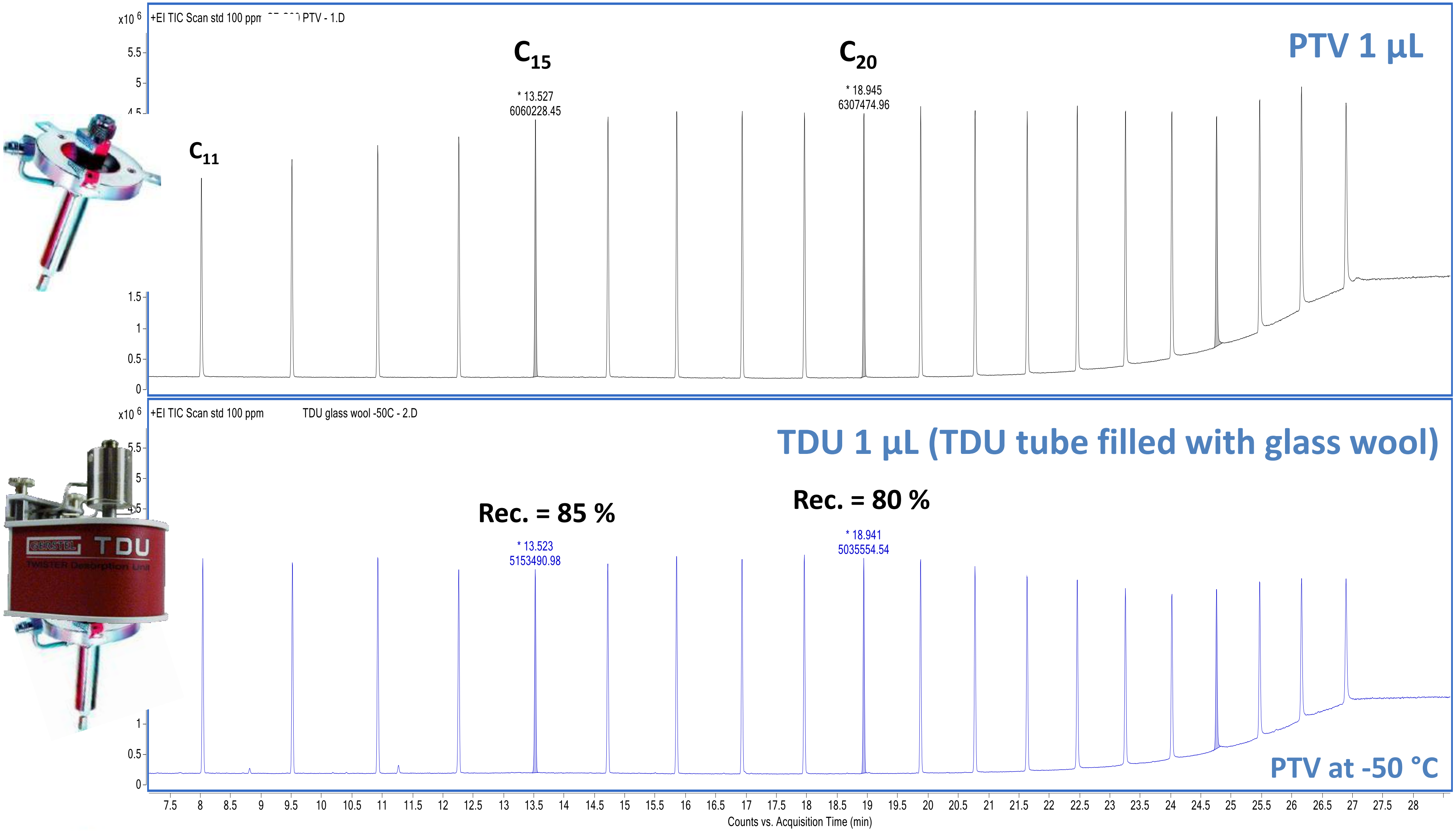
SBSE

Thermal extraction (TE)

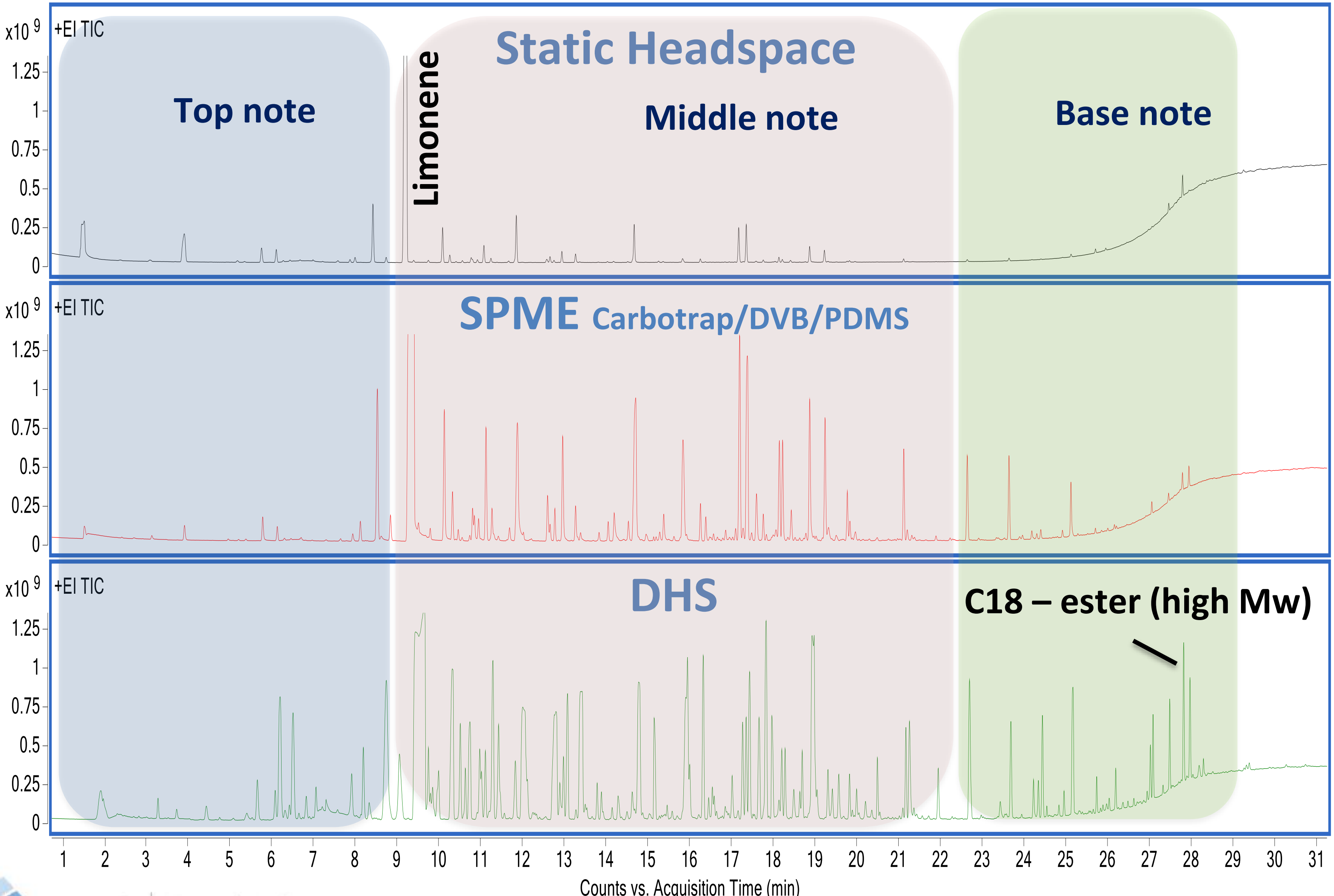
And

DHS Analysis… !!

Liquid injection: Standard PTV inj. versus Liquid TDU-PTV



Method comparison for Fruit drink



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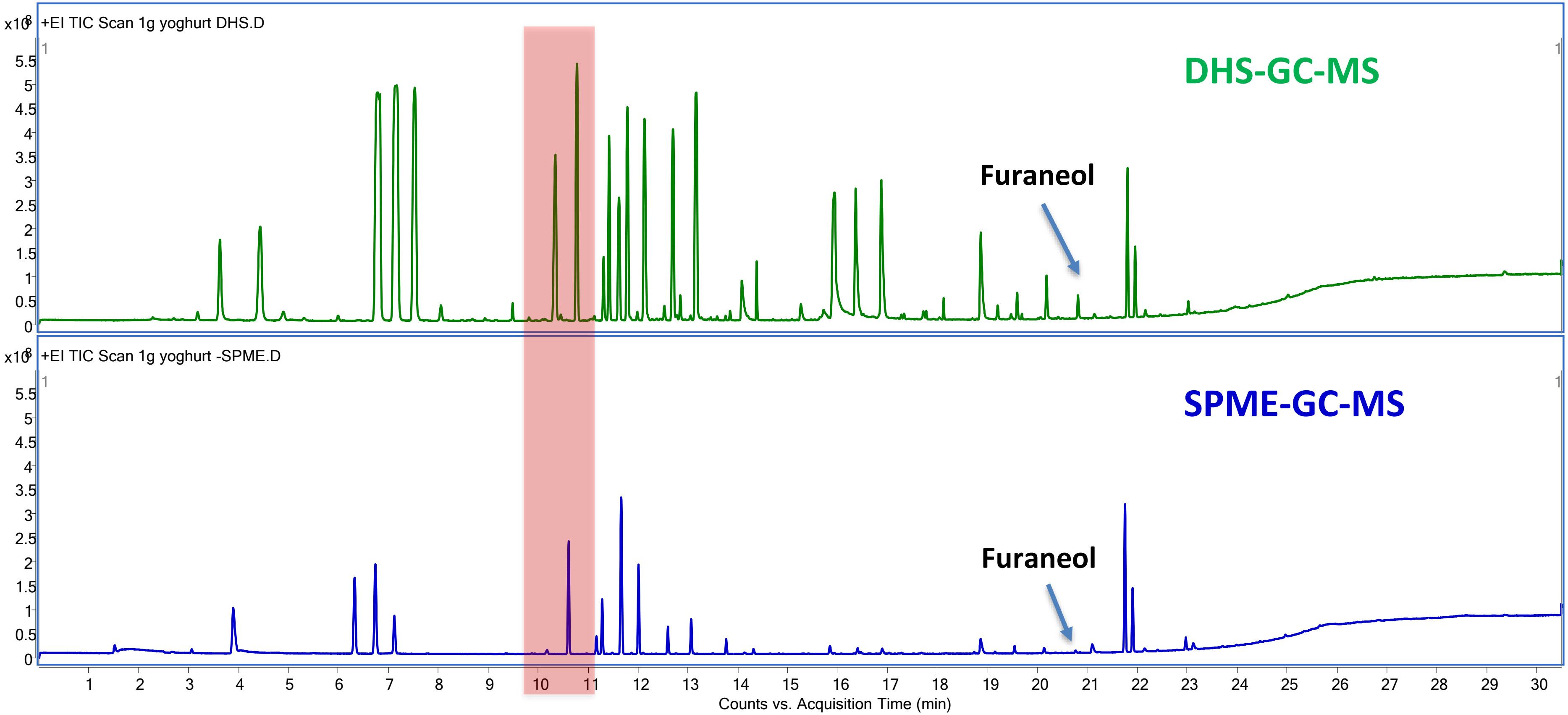
DHS vs SPME: Yoghurt (Strawberry aroma spiked)

1g yoghurt in 20 mL vial



Trans-hexenal detected @ 10.45 min by DHS and not by SPME

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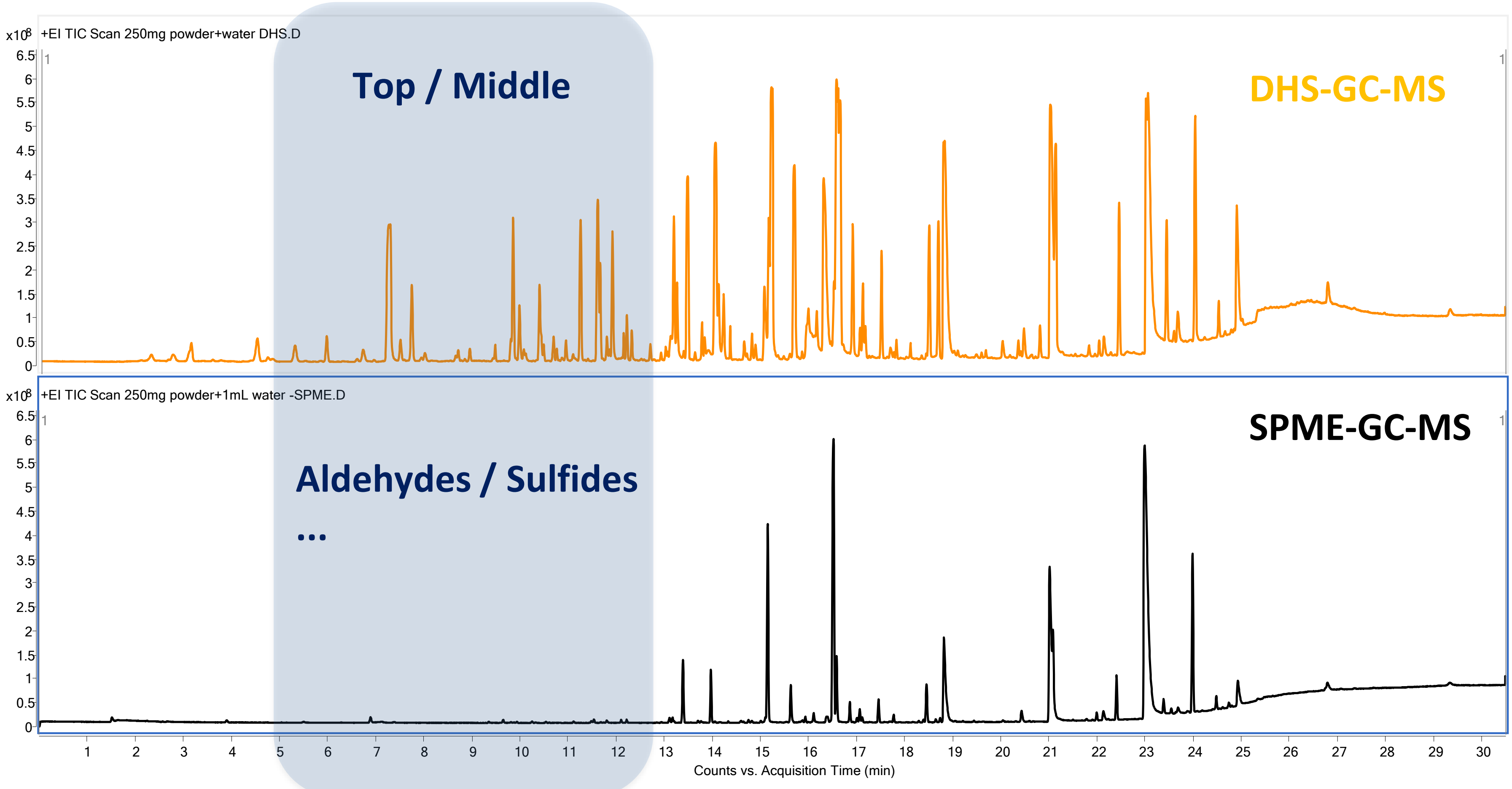
DHS vs SPME: Beef powder

250mg powder with 1 mL water in 20 mL vial



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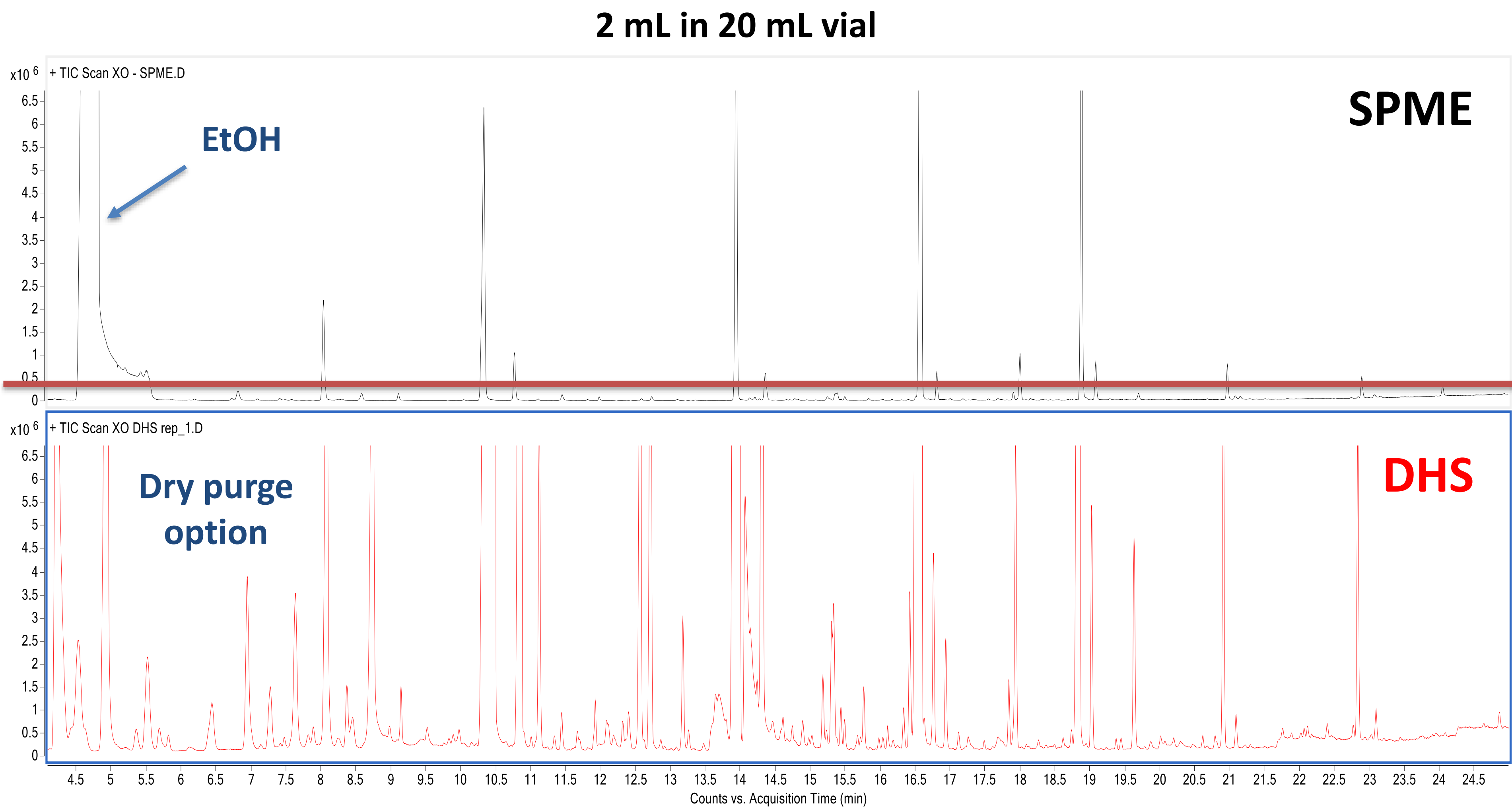
DHS vs SPME: Cognac XO (Extra Old !!)



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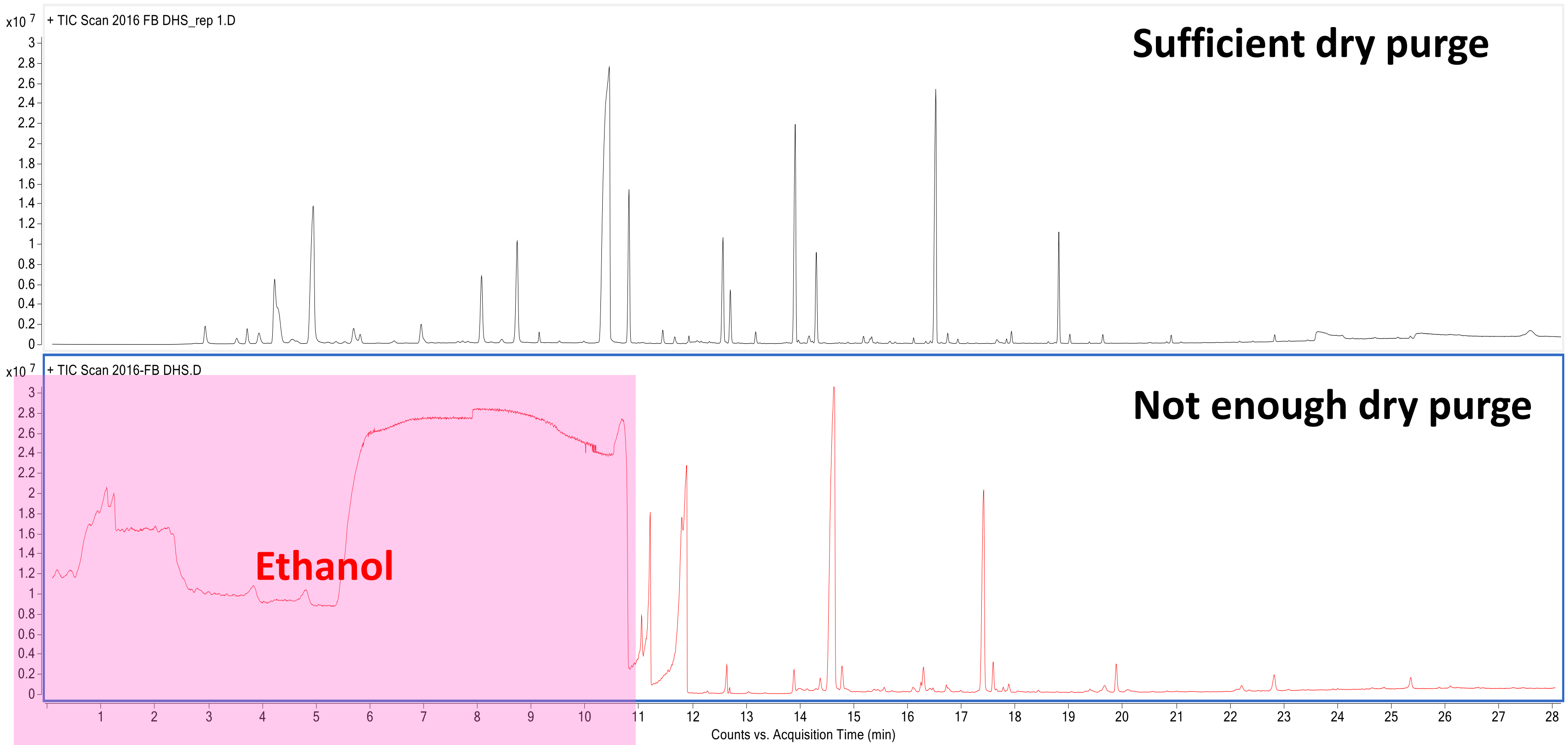
DHS-GC-MS: importance of dry purge option

Cognac XO



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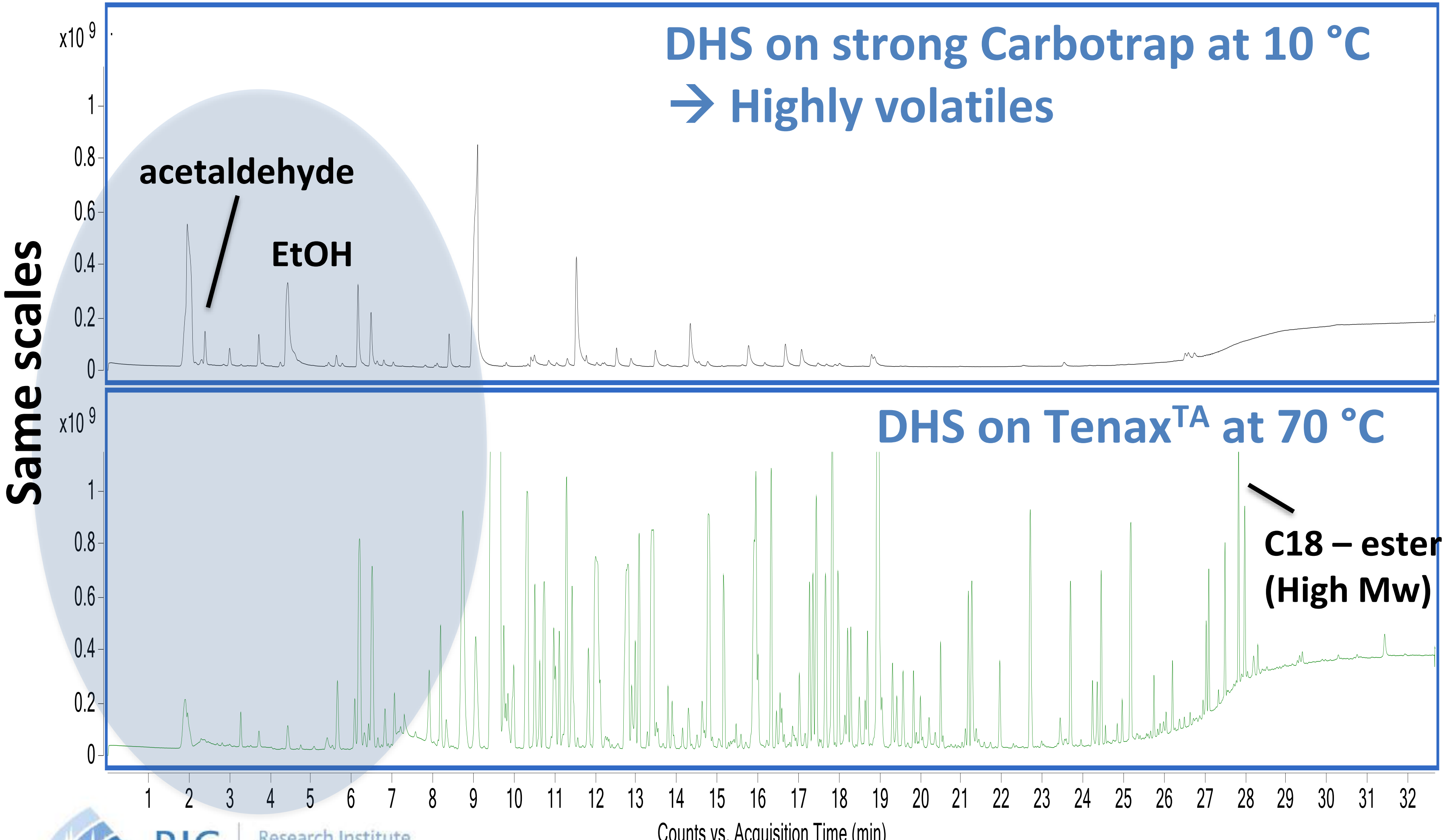
DHS modes of operation

- **Conventional DHS: single extraction – single run**
  - Tenax or Carbotrap (#) adsorption tube
  - without/with dry purge - offline (DHS)/online (TDU solvent vent) dry purge
- FEDHS: Full Evaporation DHS
- MVM: Multi-Volatile Method
  - Multiple tubes & DHS sampling
  - Desorption & trapping
  - Single GC run
- Derivatization-DHS
- DHS / CTS-2 for very volatile compounds – sensitivity “boost”
- SE-DHS (End-Step within sample prep automation)
- DHS Large

Create complementary DHS methods for aroma compounds in food and beverages – Fruit drink



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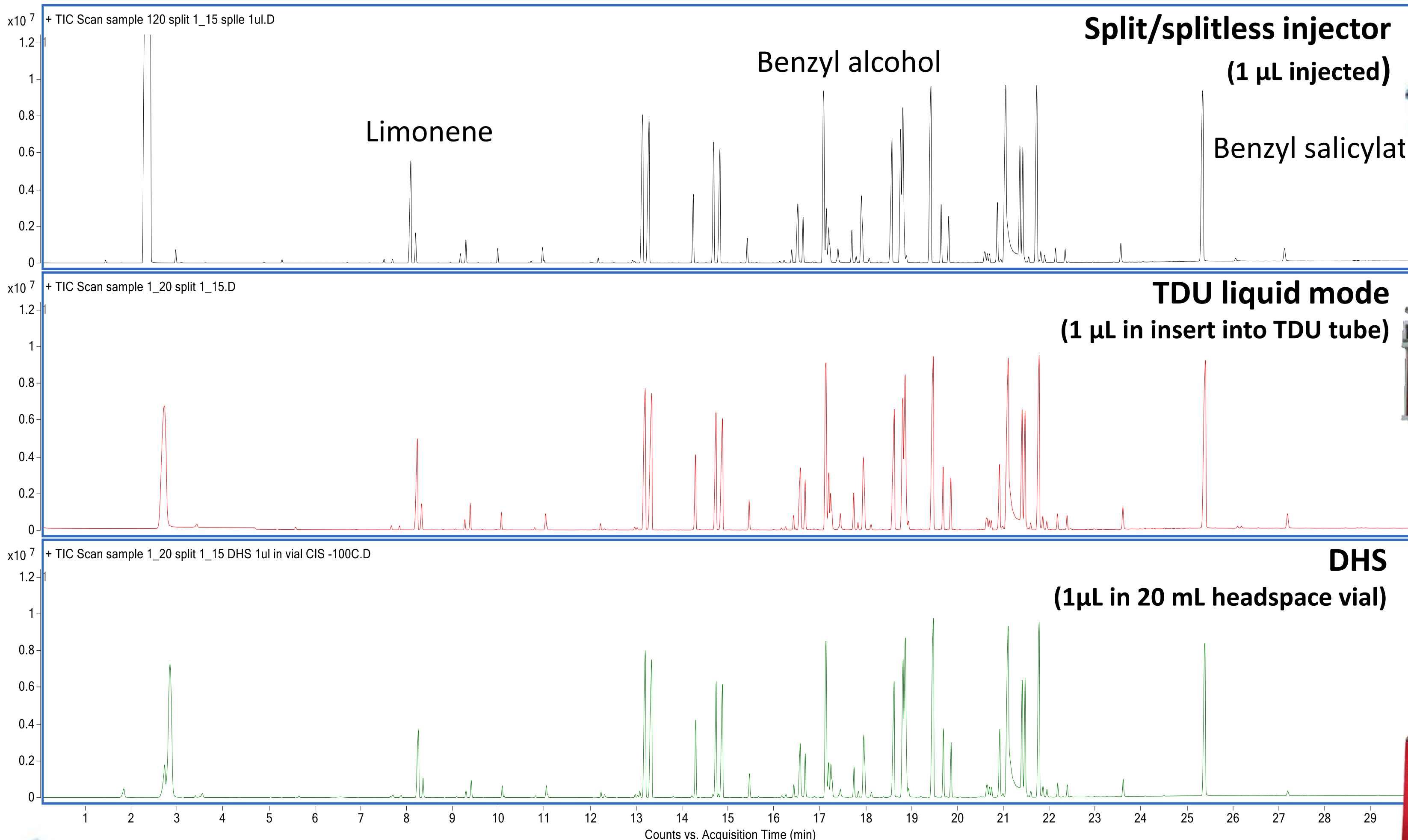
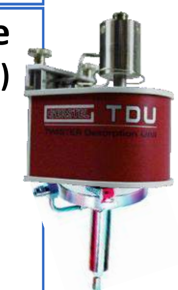
DHS can deliver similar results as liquid injection
Standard DHS method development step

1 µl 1/20 dilution of perfume in acetone – 1/15 split injection





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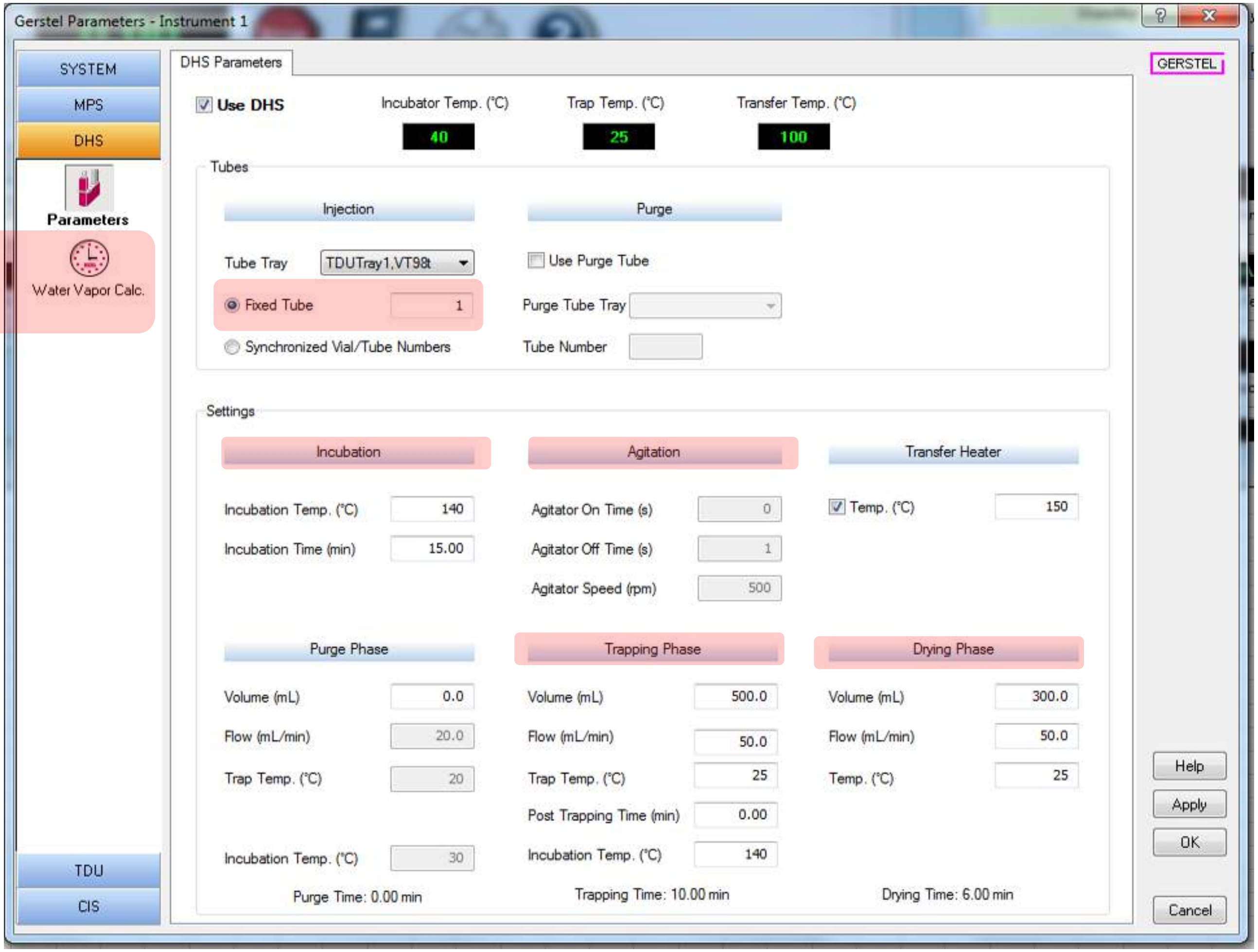
DHS parameters - Flexibility

- Extraction (classic DHS)
  - Incubation (sample) temperature (as low as possible)
  - Trap:
    - Material
    - Temperature (higher = less water)
  - Time & flow (= x rinses of vial volume)
    example: 500 mL volume, 50 mL/min = 10 min = 25 rinses
  - Dry purge ??? (loss of volatiles)
- TDU: desorption temperature (time, flow, temperature)
- CIS:
  - Focusing temperature (w/ packing?)
  - Injection mode (split, splitless)
  - Injection temperature
- CTS 2 refocusing

DHS parameters in Maestro



Water Vapor Calc.

Calculates the amount of water on the tube after x mL of purge volume during DHS enrichment

pV = nRT let's us calculate the minimum dry purge volume

Breakthrough volume is very low for water on Tenax and Carbo based desorption tubes

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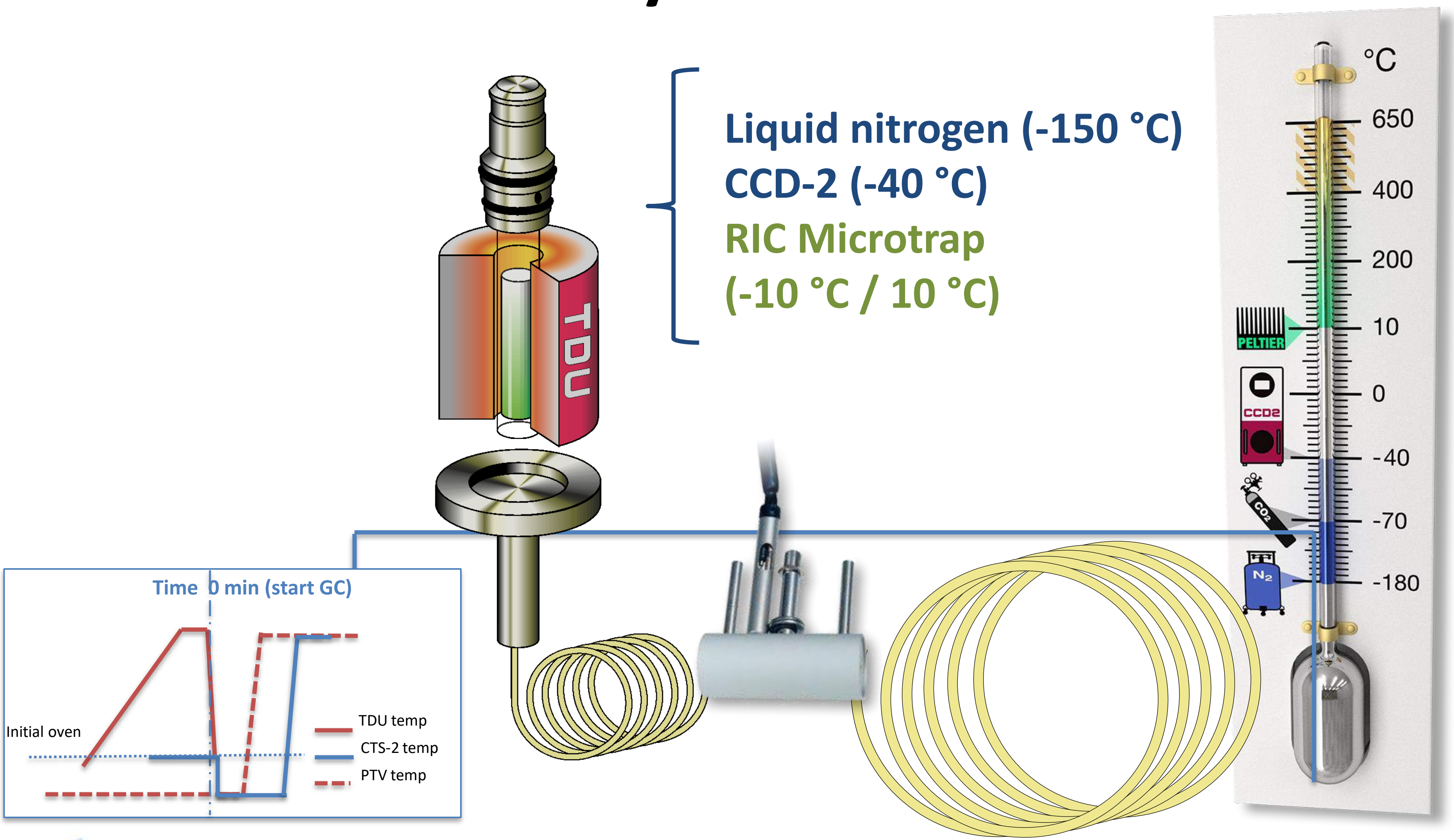
Dynamic Headspace + CTS-2 trapping
Very Volatiles



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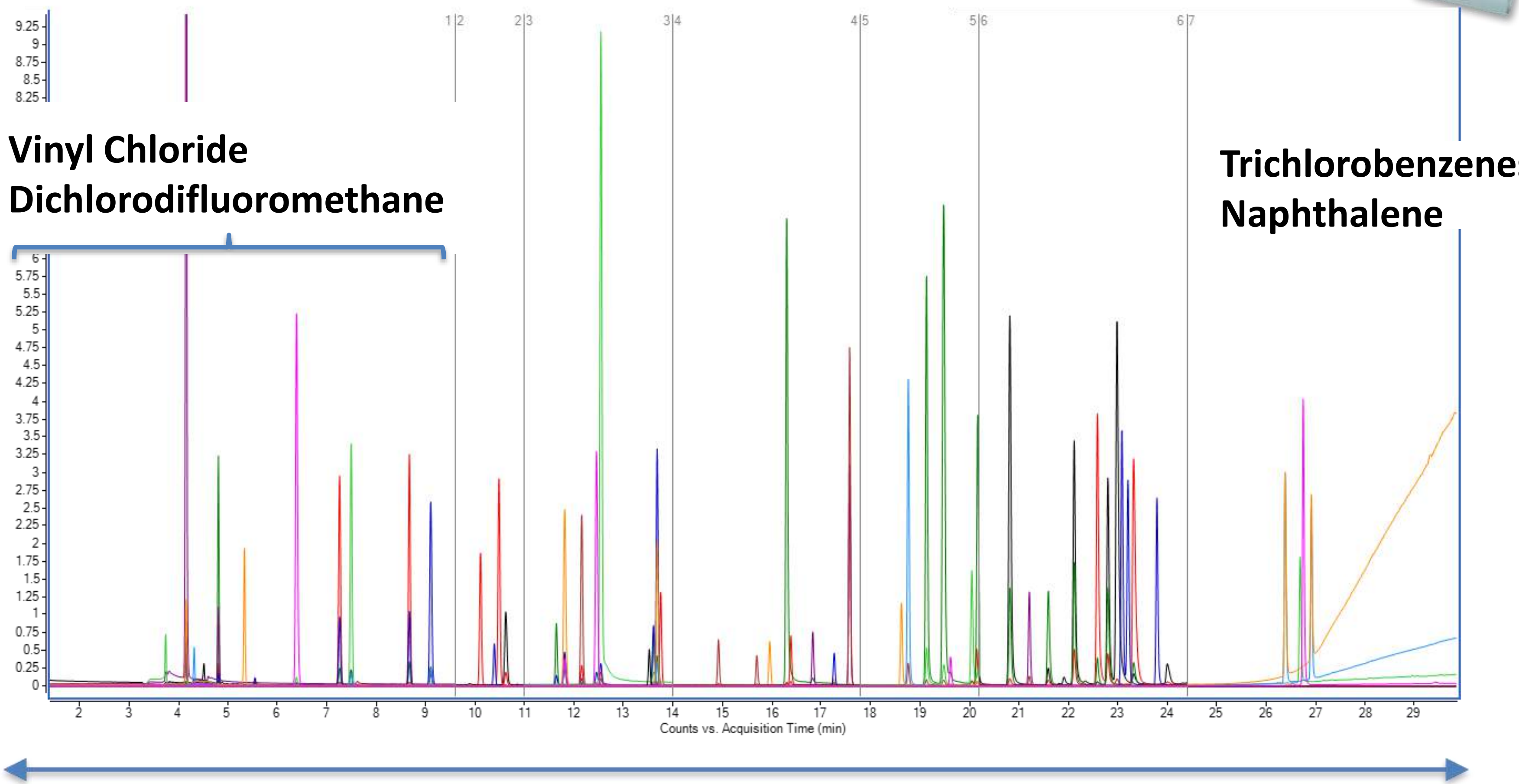
Dynamic Headspace + CTS-2 trapping
Very Volatiles



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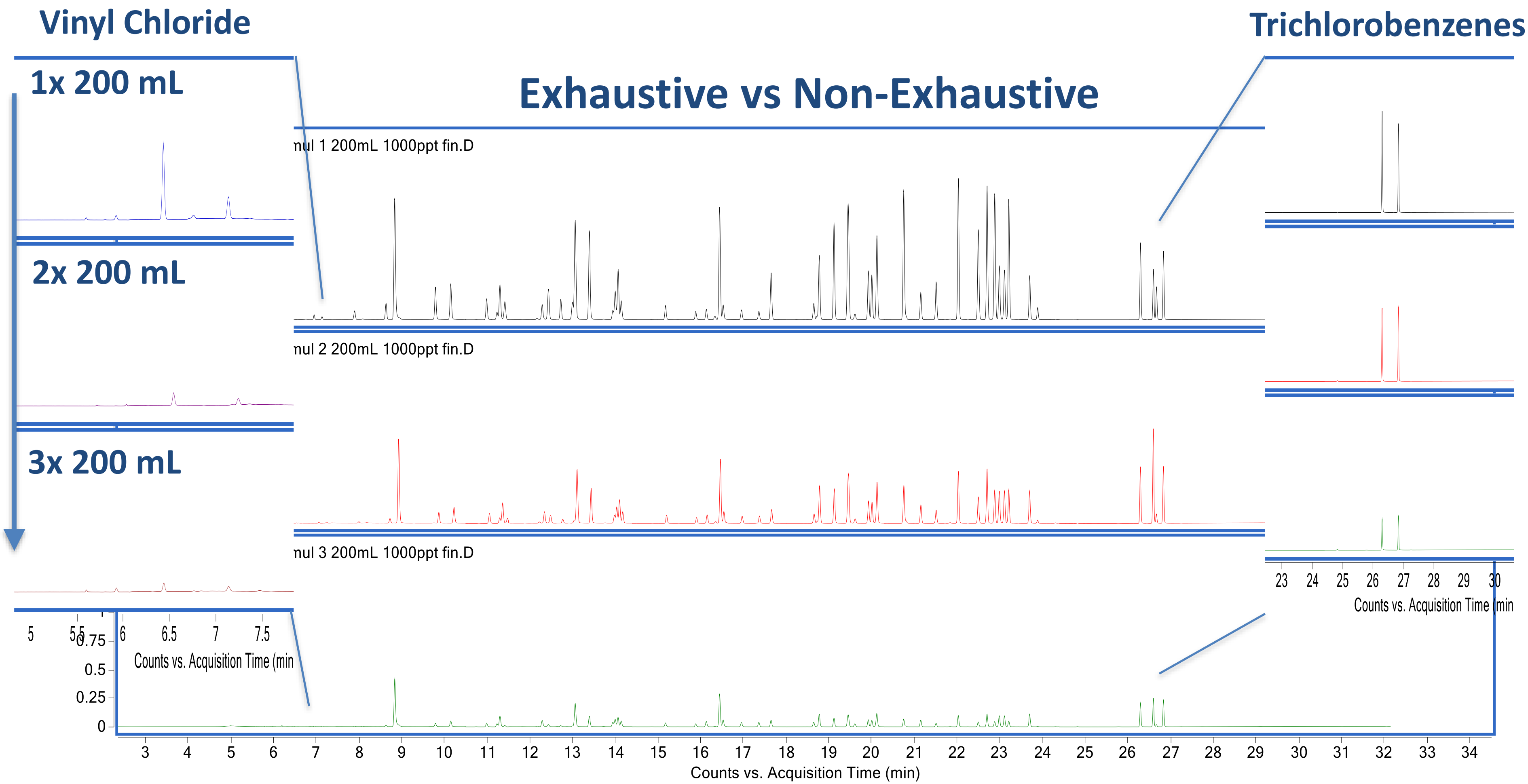
Dynamic Headspace (+ CTS-2)
Very Volatiles 1000 ppt / 10 mL of water sample



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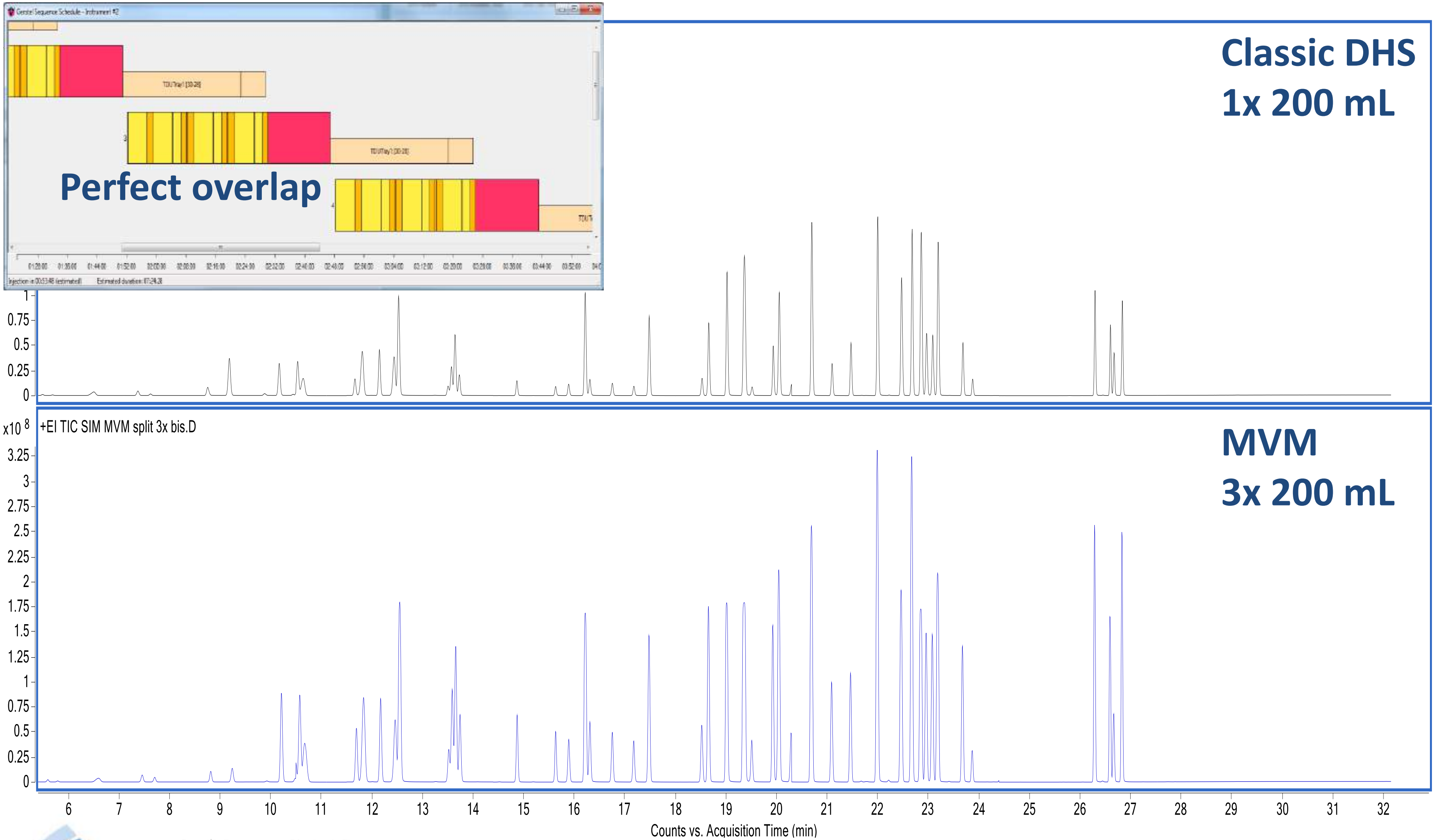
Dynamic Headspace (+ CTS-2)
MVM will avoid breakthrough



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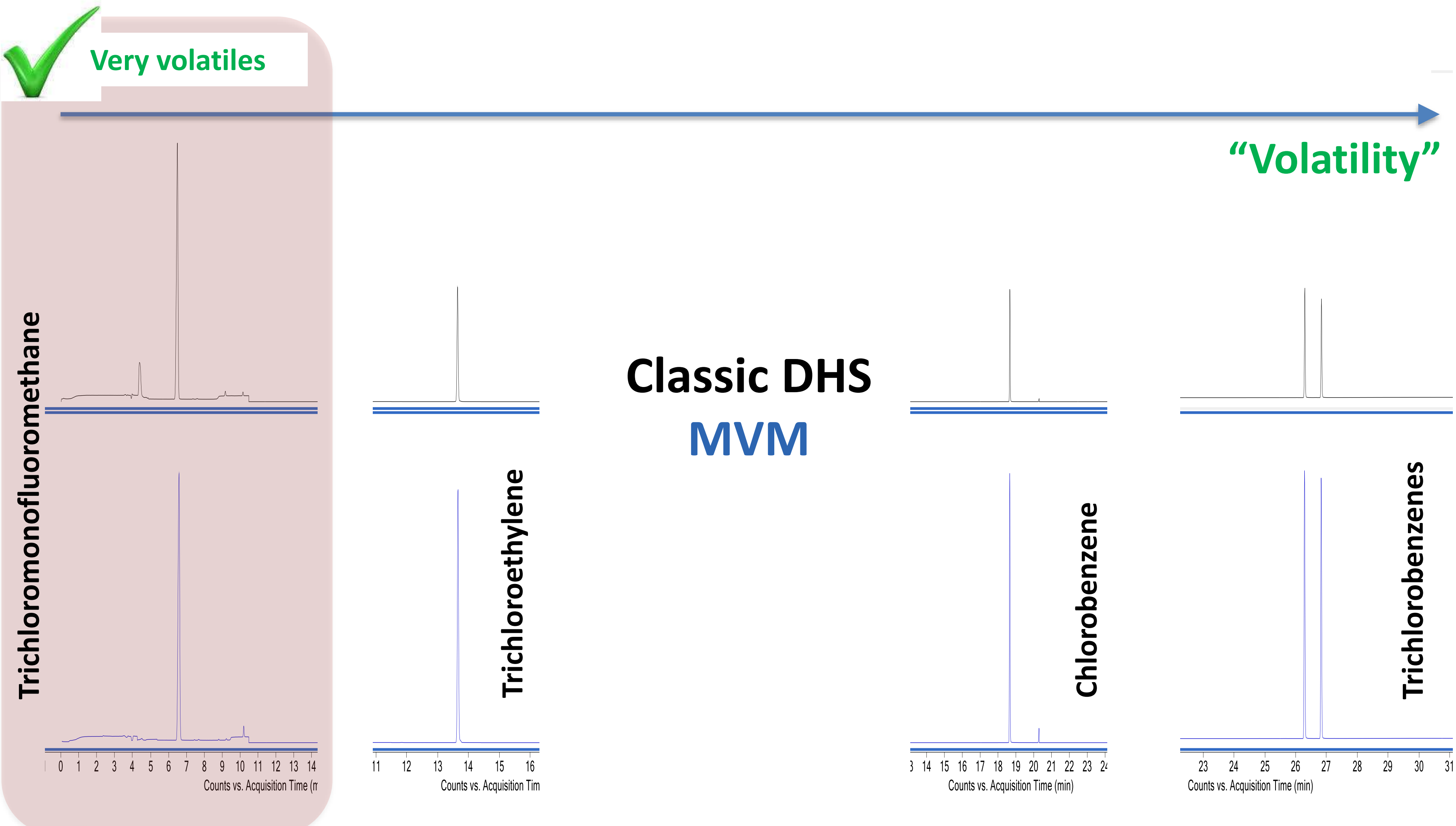
Dynamic Headspace (+ CTS-2)
„Exhaustive“ enrichment / higher sensitivity



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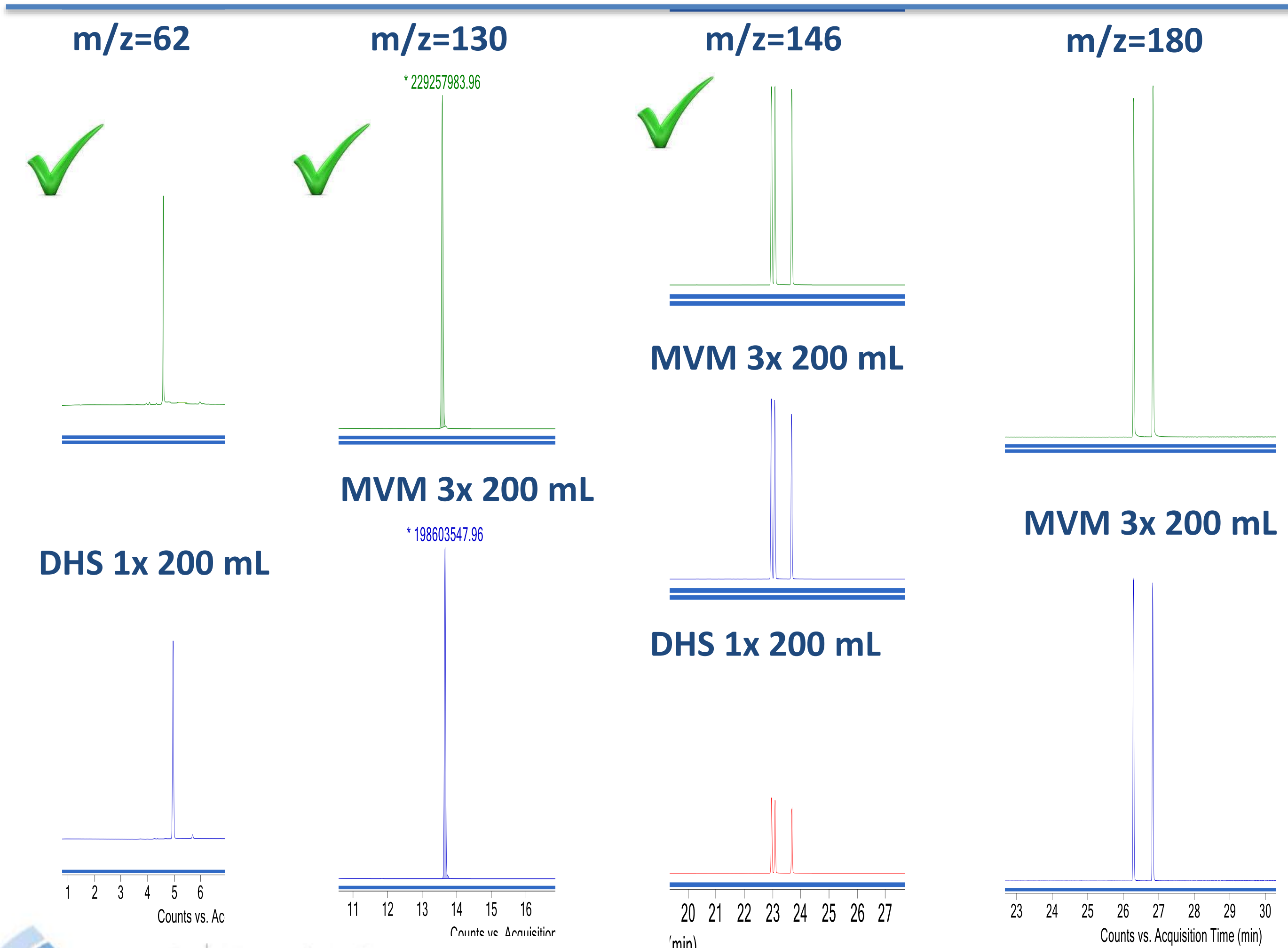
Dynamic Headspace (+ CTS-2)
„Exhaustive“ enrichment / higher sensitivity

Vinyl Chloride | Trichloroethylene | Dichlorobenzenes | Trichlorobenzenes



Reference (Spike on TD Tube)

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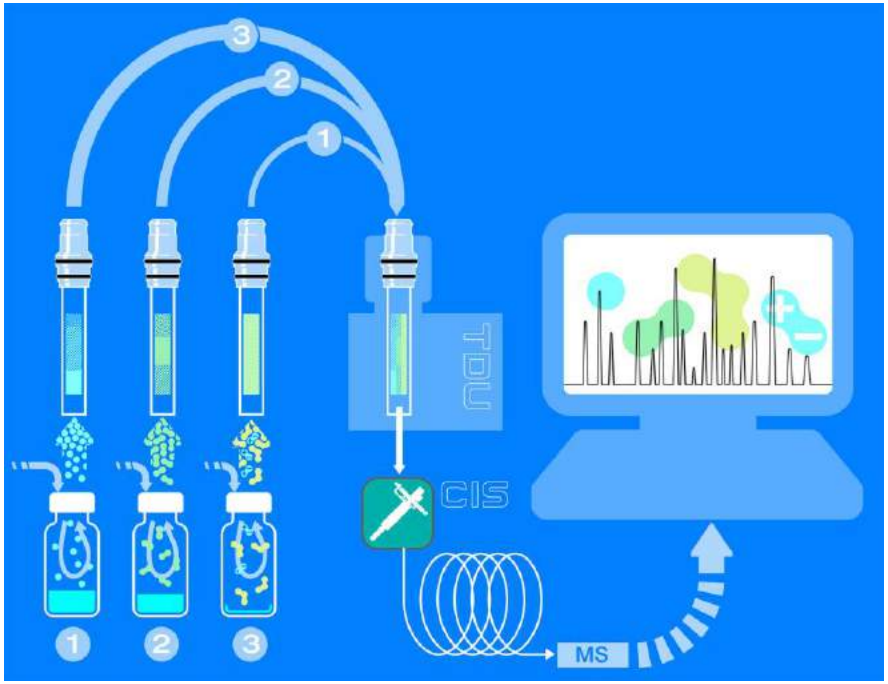
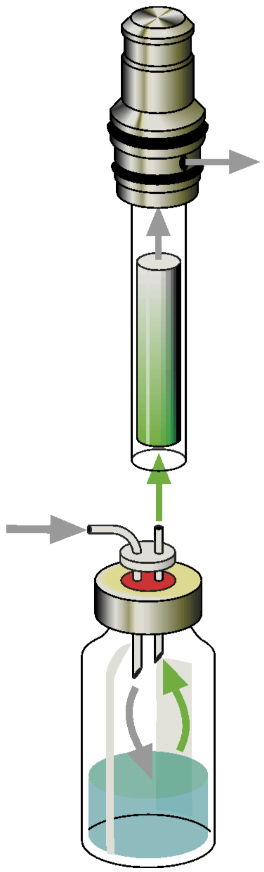
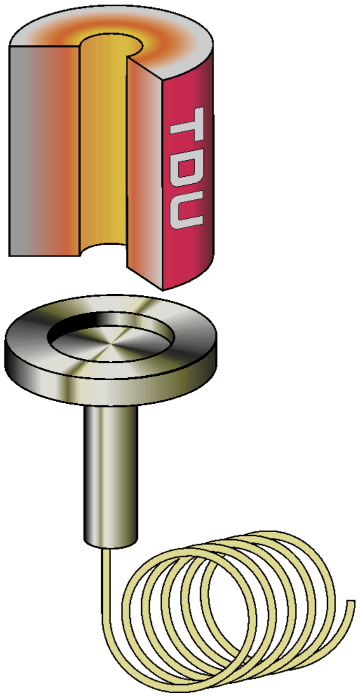
Sequential Dynamic Headspace Sampling
Multi-Volatile Method (MVM)



Dynamic Headspace
Method 1: Very Volatile Analytes

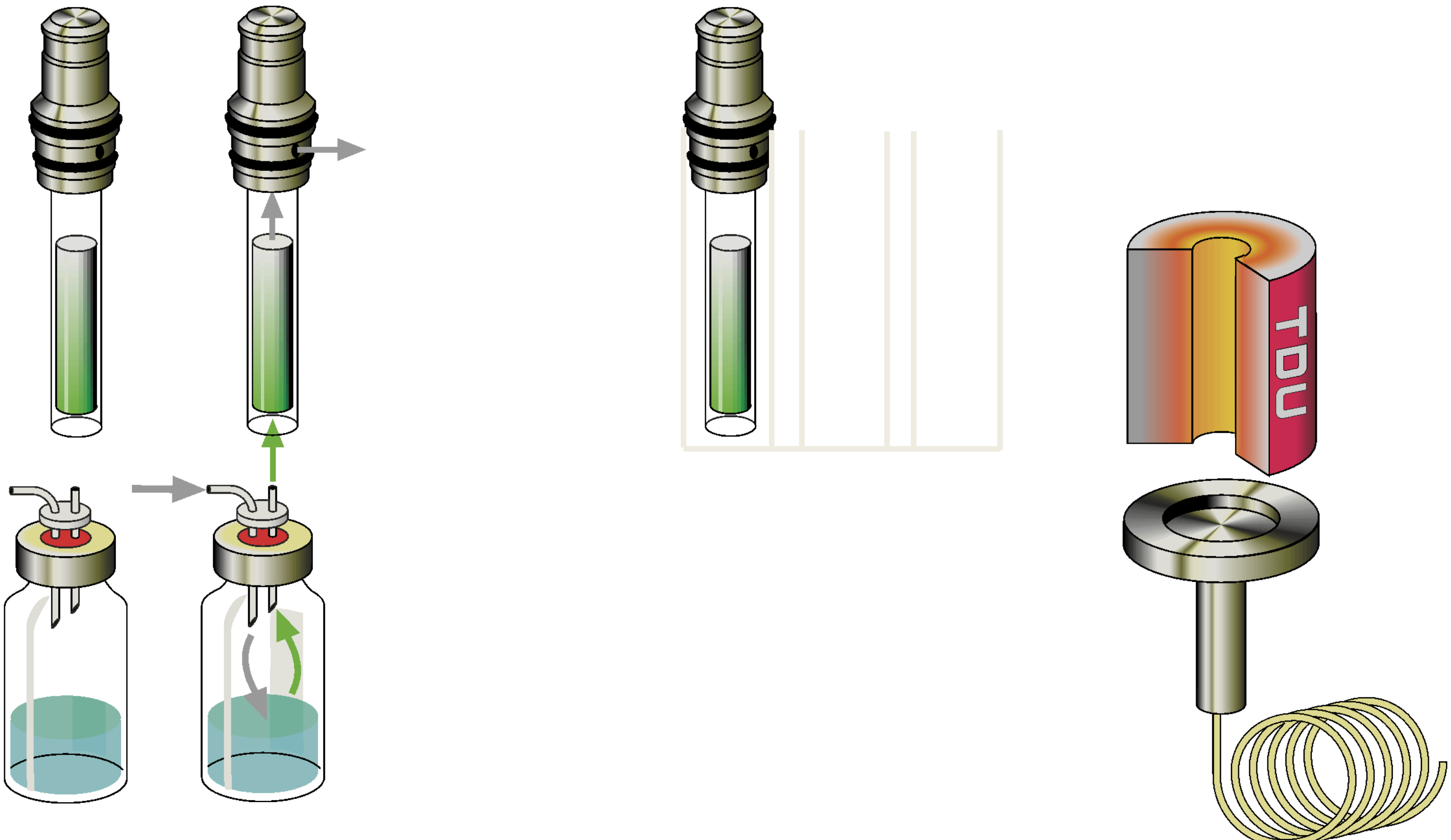




(J. Tsunokawa, N. Ochiai, K. Sasamoto, A. Hoffmann, in preparation)

Dynamic Headspace

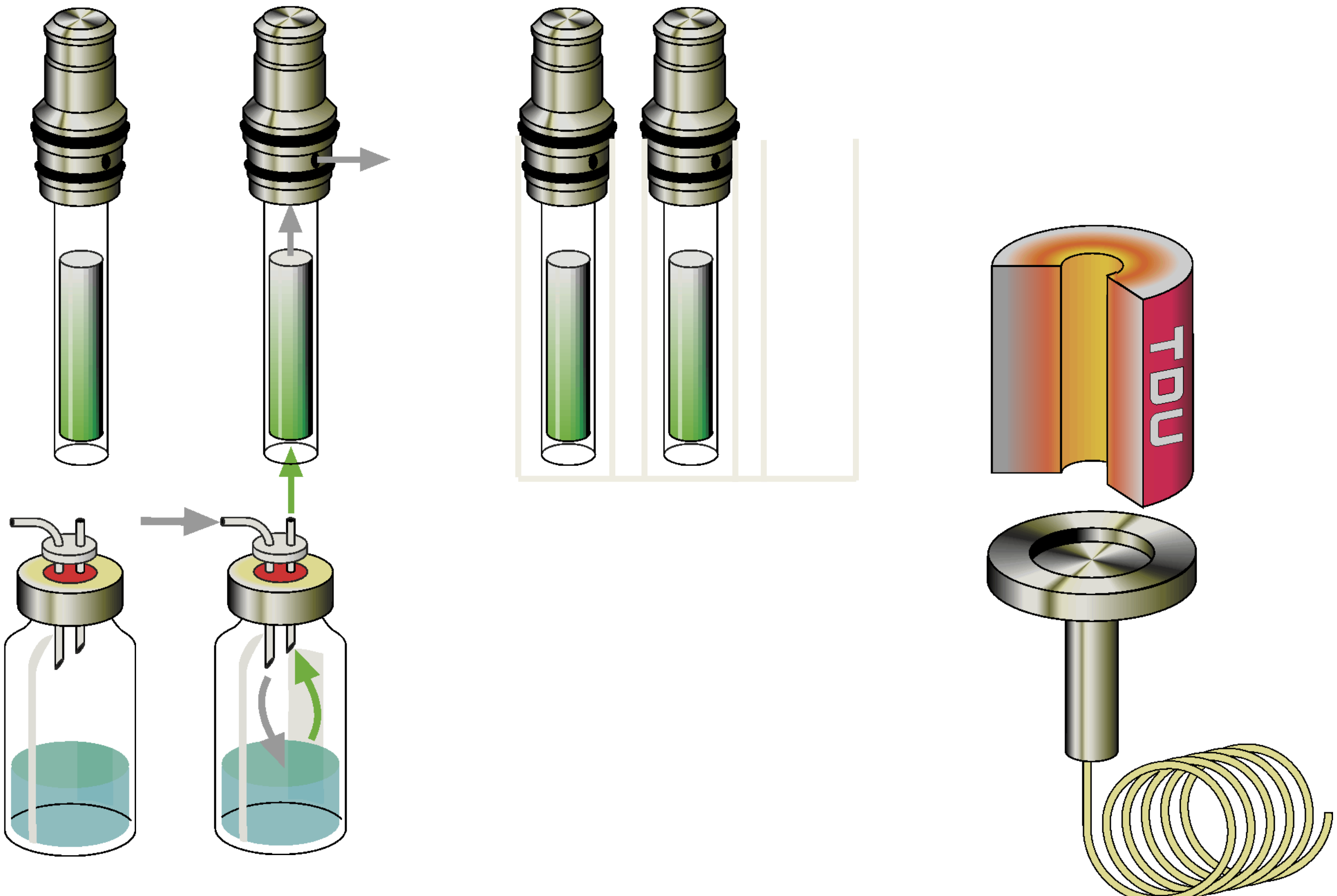
Method 1: Very Volatile Analytes
Method 2: Volatile to Semi Volatile Analytes



(J. Tsunokawa, N. Ochiai, K. Sasamoto, A. Hoffmann, in preparation)

Dynamic Headspace
Method 3: Volatile, nonvolatile and hydrophilic analytes

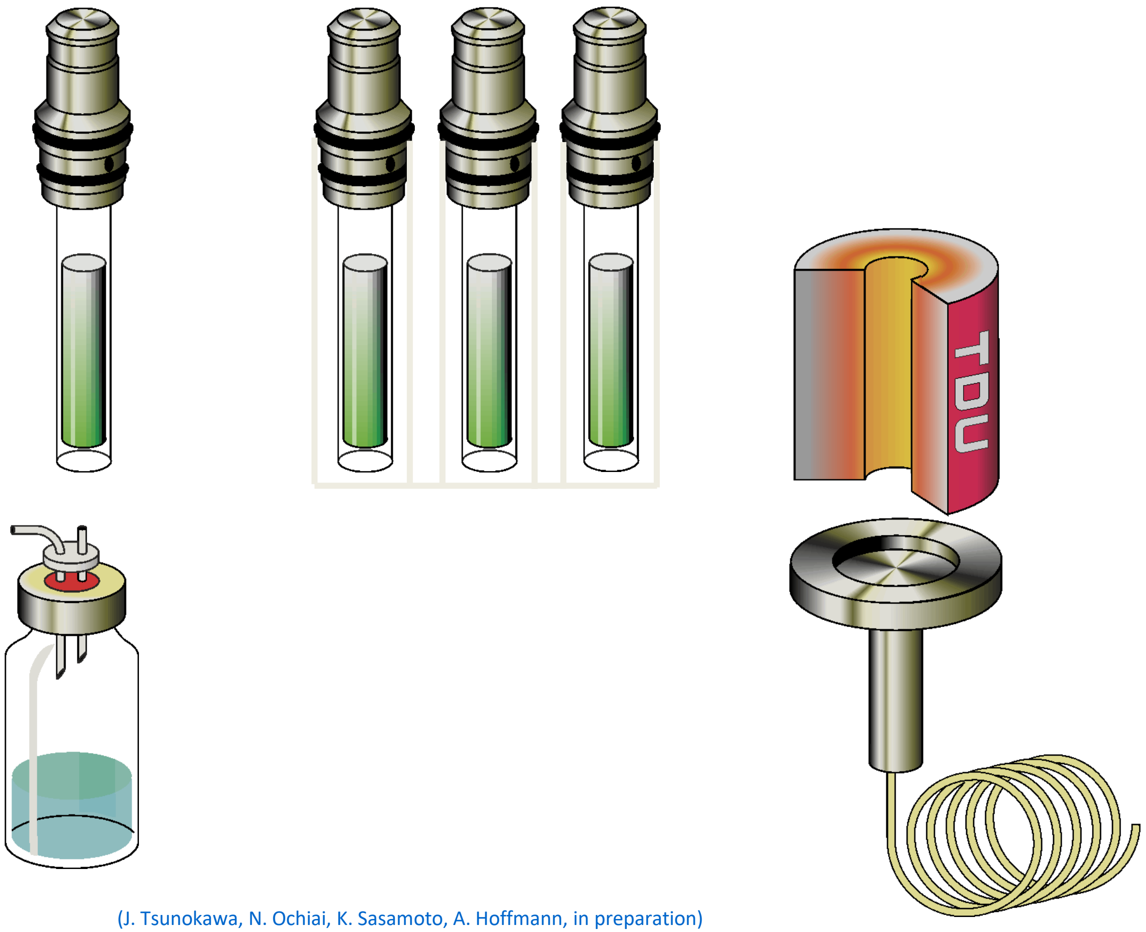
Dynamic Headspace
Method 2: Volatile or Semi-Volatile Analytes



(J. Tsunokawa, N. Ochiai, K. Sasamoto, A. Hoffmann, in preparation)

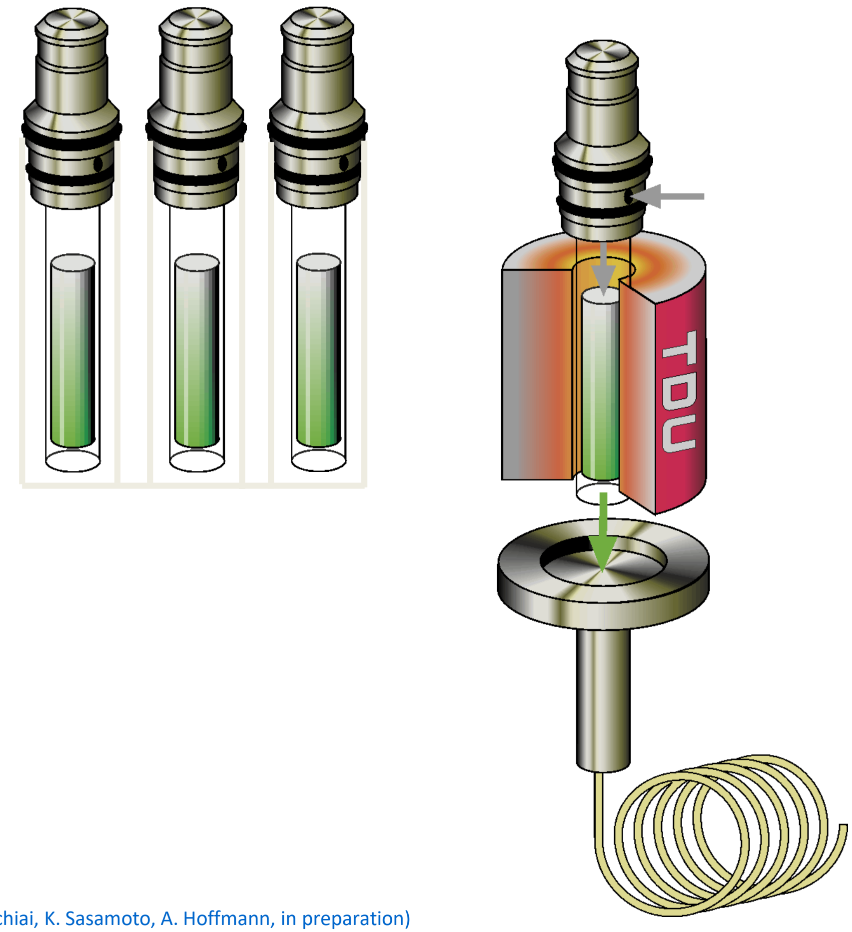
Dynamic Headspace

Method 3: Volatile, non volatile and hydrophillic analytes



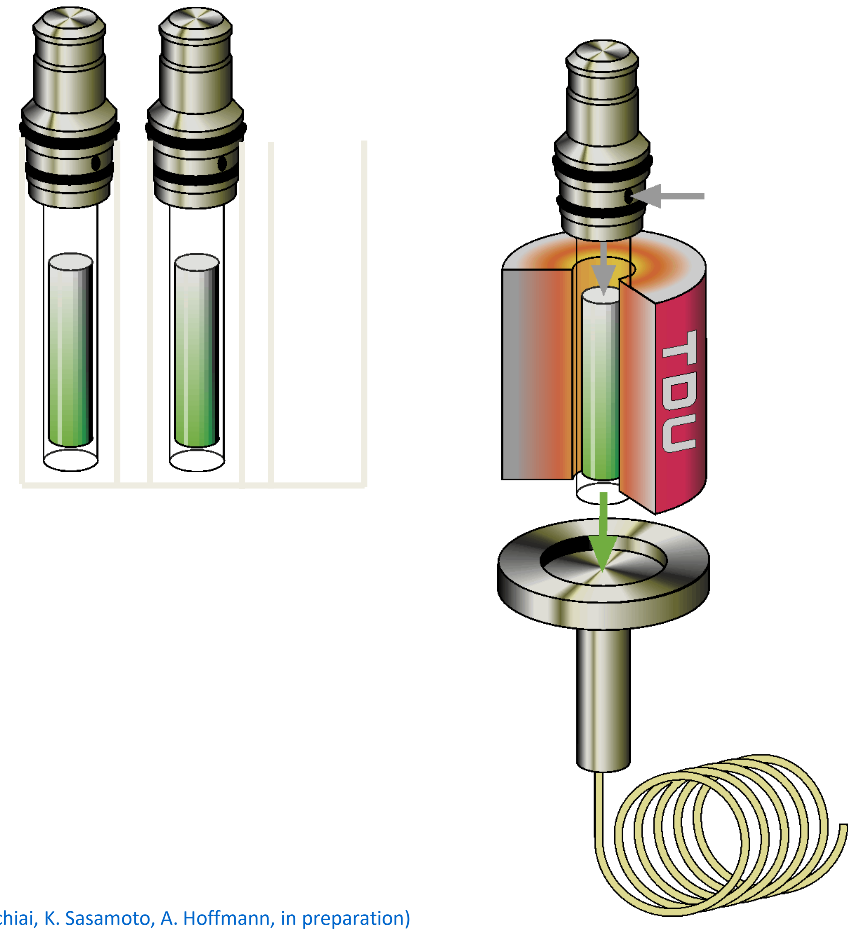
(J. Tsunokawa, N. Ochiai, K. Sasamoto, A. Hoffmann, in preparation)

Dynamic Headspace
Method 4: TDU Multi Desorption



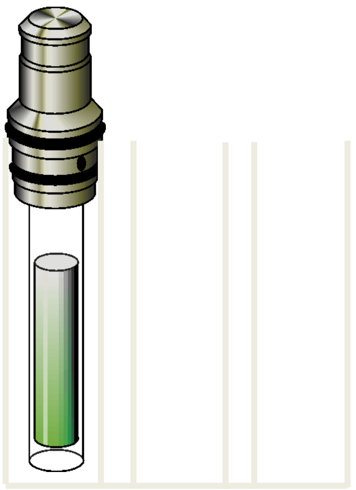
(J. Tsunokawa, N. Ochiai, K. Sasamoto, A. Hoffmann, in preparation)

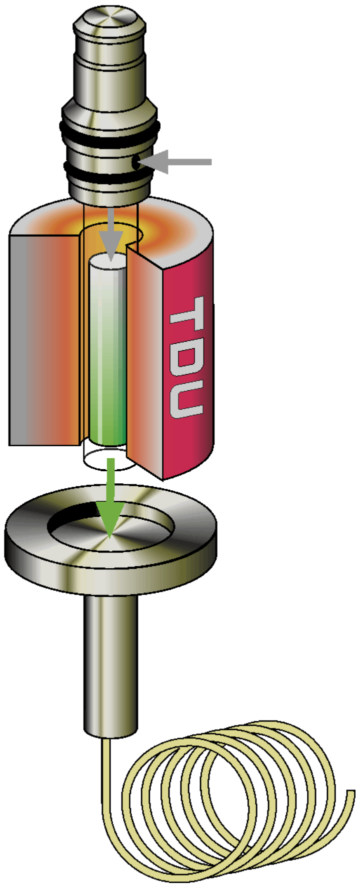
Dynamic Headspace
Method 4: TDU Multi Desorption



(J. Tsunokawa, N. Ochiai, K. Sasamoto, A. Hoffmann, in preparation)

Dynamic Headspace
Method 4: TDU Multi Desorption



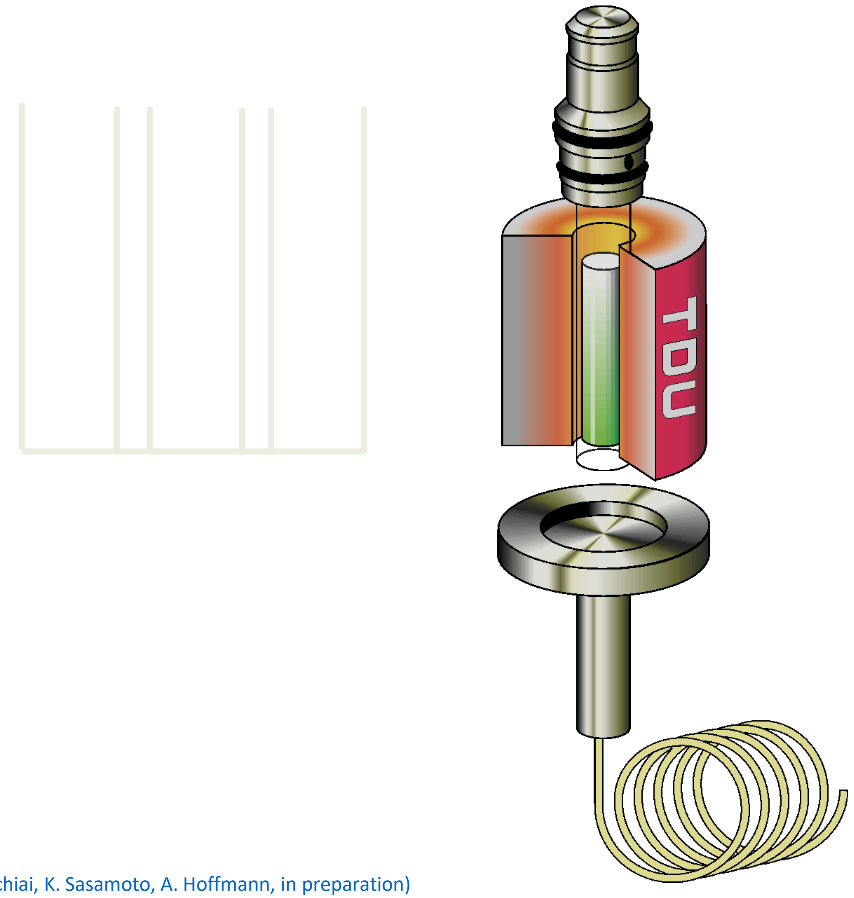


Different PTV initial temperature

Different TDU Desorption Gradient

(J. Tsunokawa, N. Ochiai, K. Sasamoto, A. Hoffmann, in preparation)

Dynamic Headspace
Method 4: TDU Multi Desorption



(J. Tsunokawa, N. Ochiai, K. Sasamoto, A. Hoffmann, in preparation)

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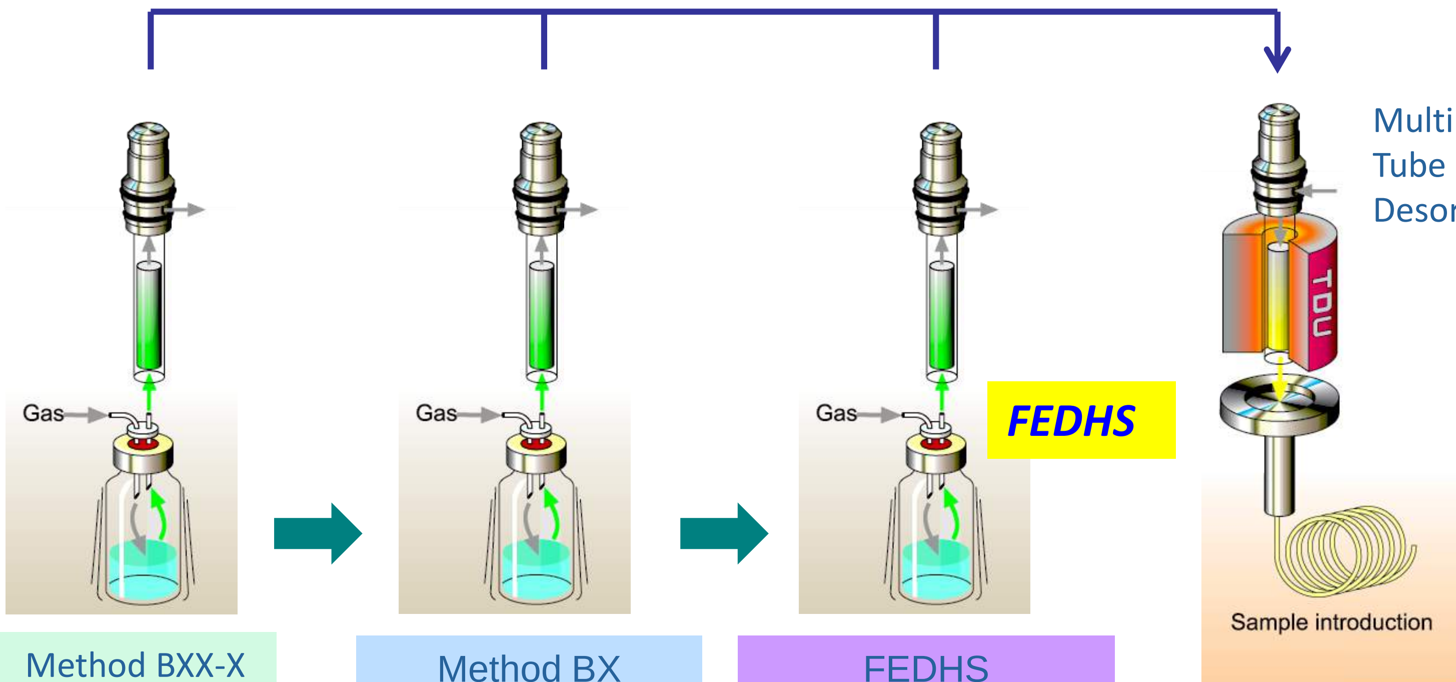
DHS-Multi-Volatile Method (DHS-MVM ®)*

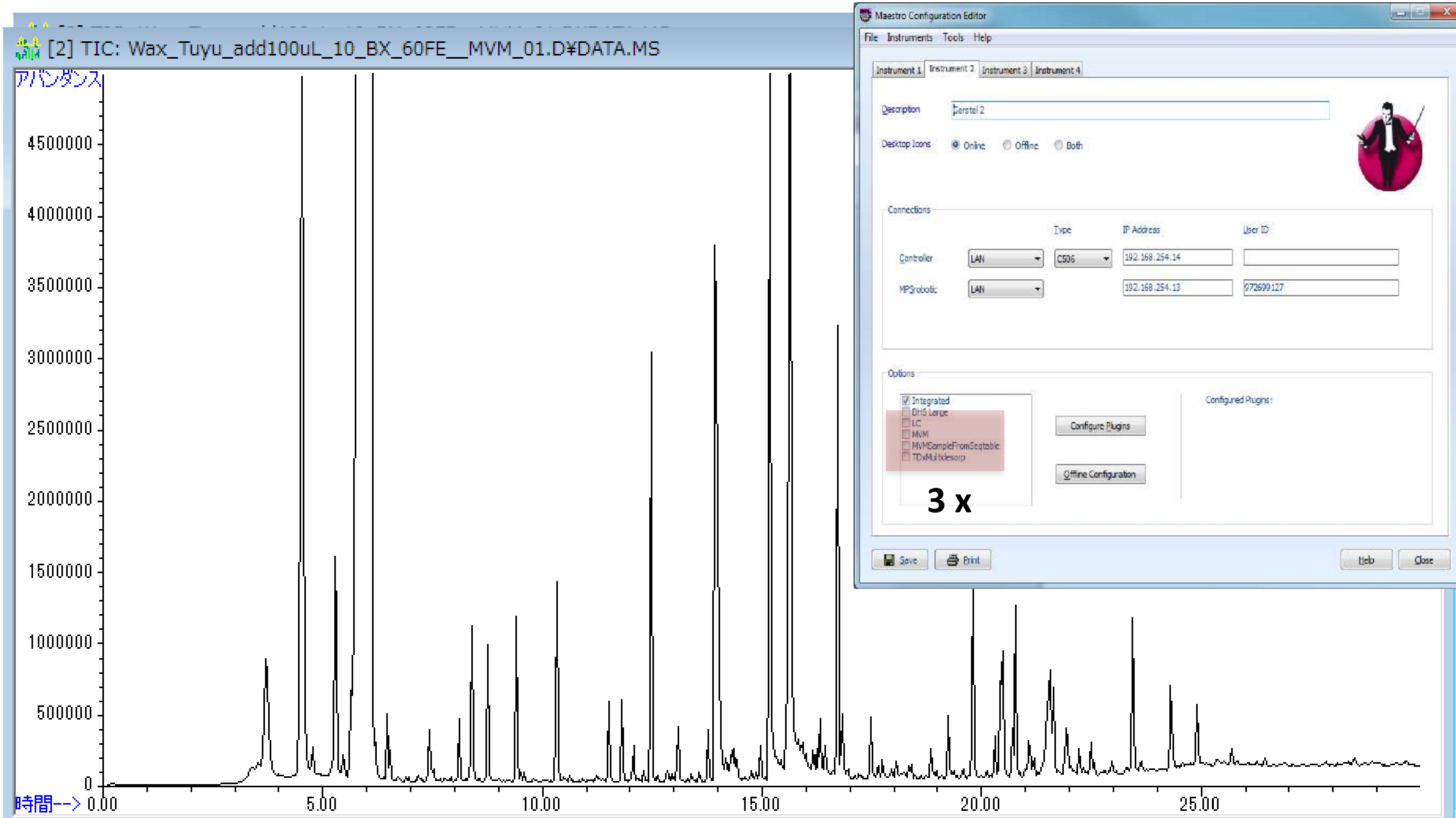
"MVM option"
(Maestro 1.4.29.21 or later)



Method BXX-X Shincarbon trap Top notes	Method BX Carbotrap B & X Top to middle note	FEDHS Tenax TA trap Middle to base note	
Optimized for enrichment of super VOC and top notes	Optimized for enrichment of remaining top notes to middle notes	Optimized for enrichment of remaining middle notes to base notes, polar and low boiling compounds	Three TDU tube are sequentially thermal desorbed and cryo-focused on CIS, and then injection into GC-MS

* N. Ochiai, J. Tsunokawa, K. Sasamoto, A. Hoffmann, J. Chromatogr. A 1371 (2014) 65-73.

Total ion chromatogram (TIC) of noodle soup stock by MVM



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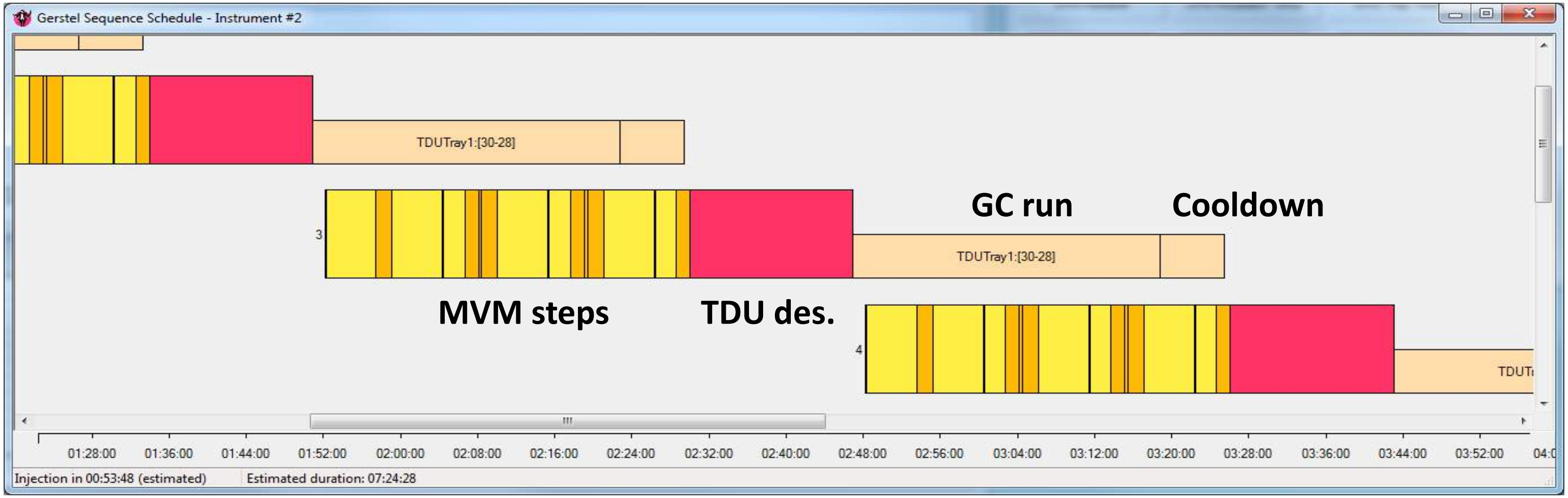
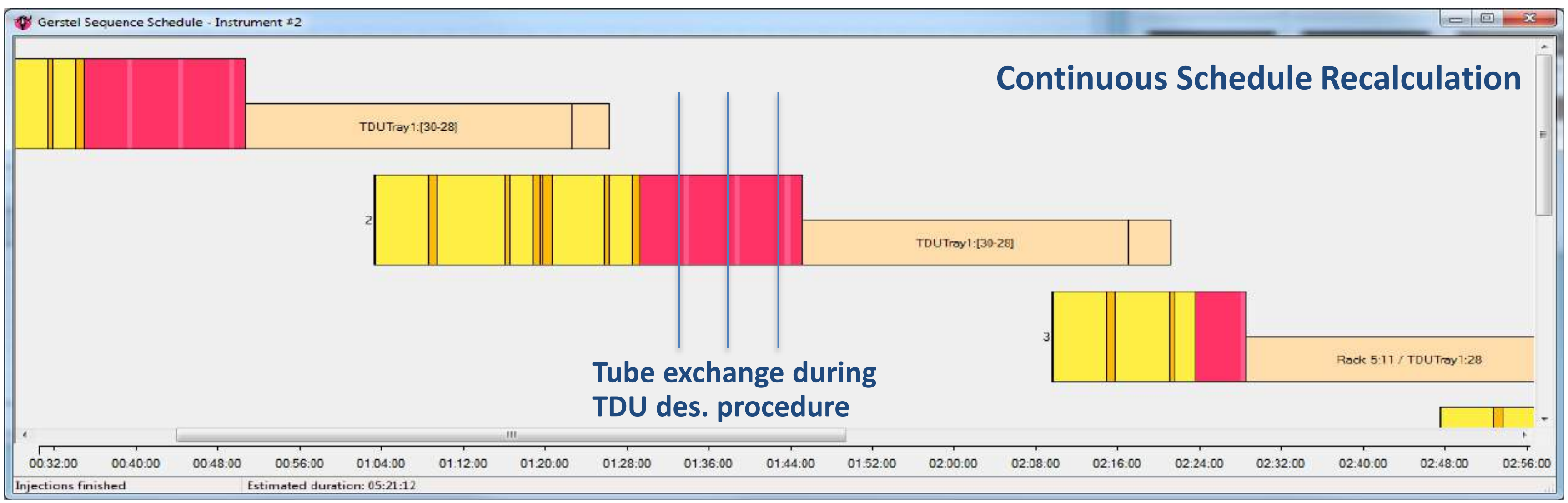
Courtesy: Gerstel KK, Japan

Maestro Scheduler for MVM





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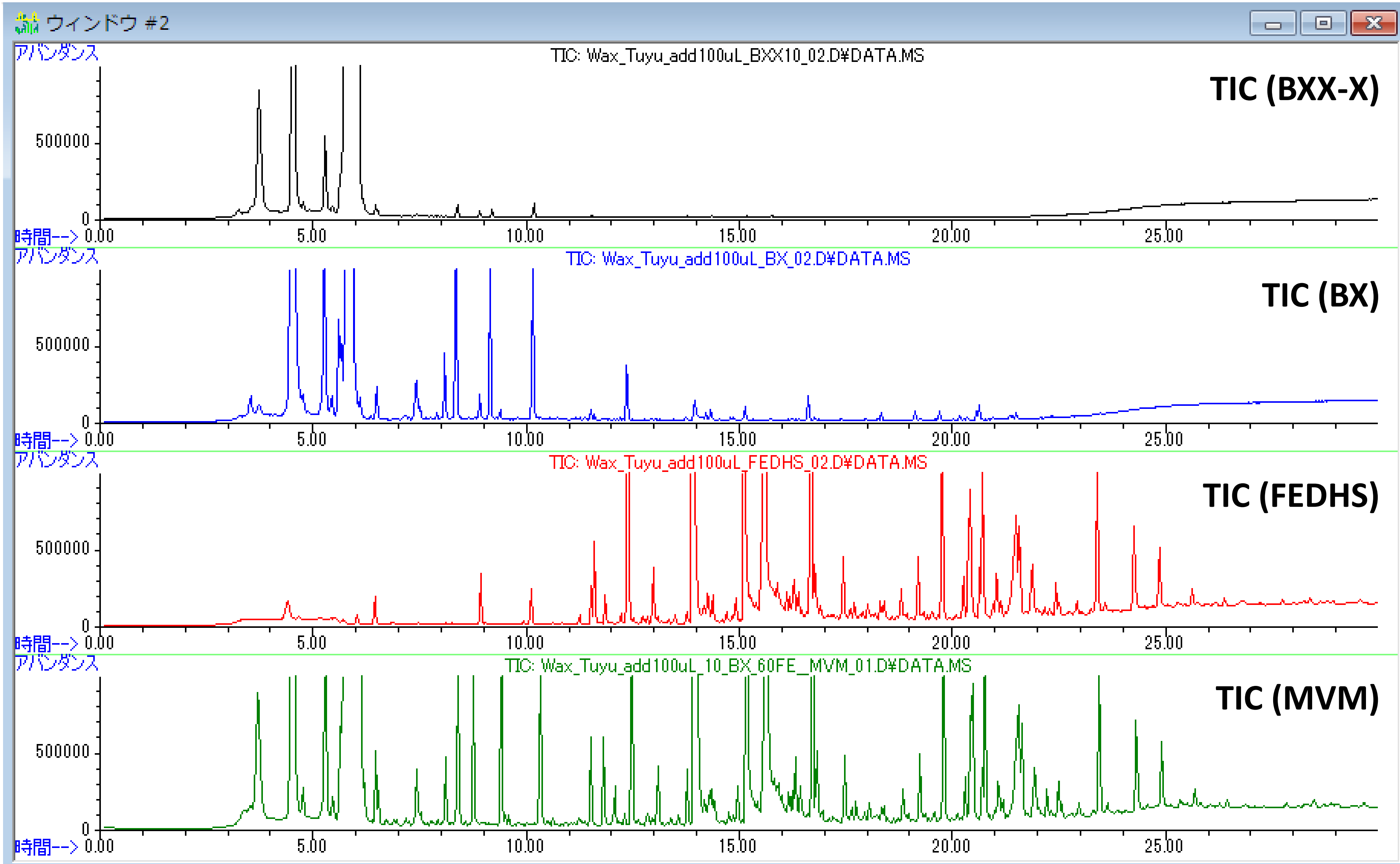
Comparison of BXX-X, BX, FEDHS and MVM for analysis of noodle soup stock



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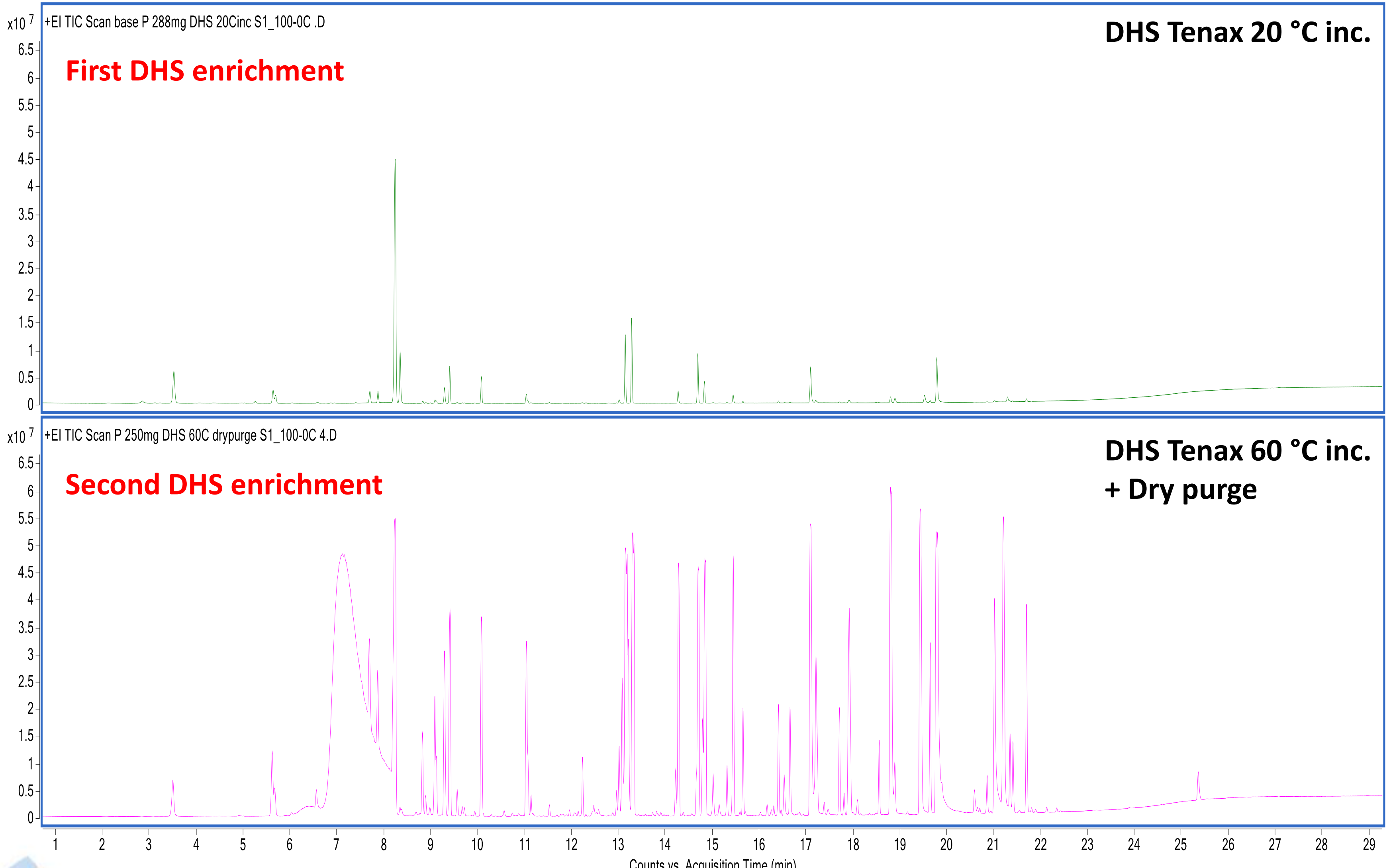
Courtesy: Gerstel KK, Japan

Method development for MVM approach

Cosmetic base → perfume added



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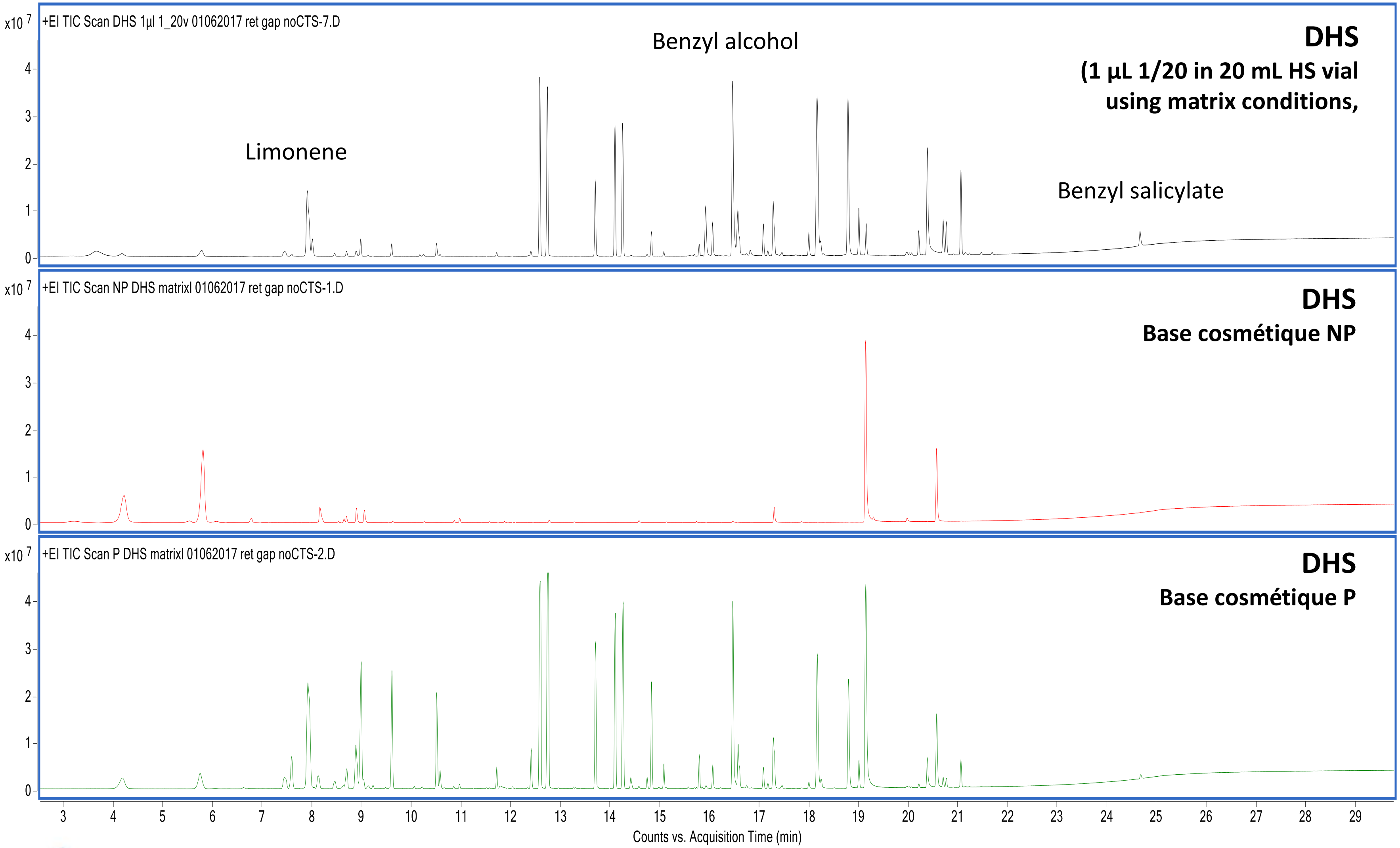
DHS TDU

200 mg matrix (cosmetic base material) in 20 mL HS vial



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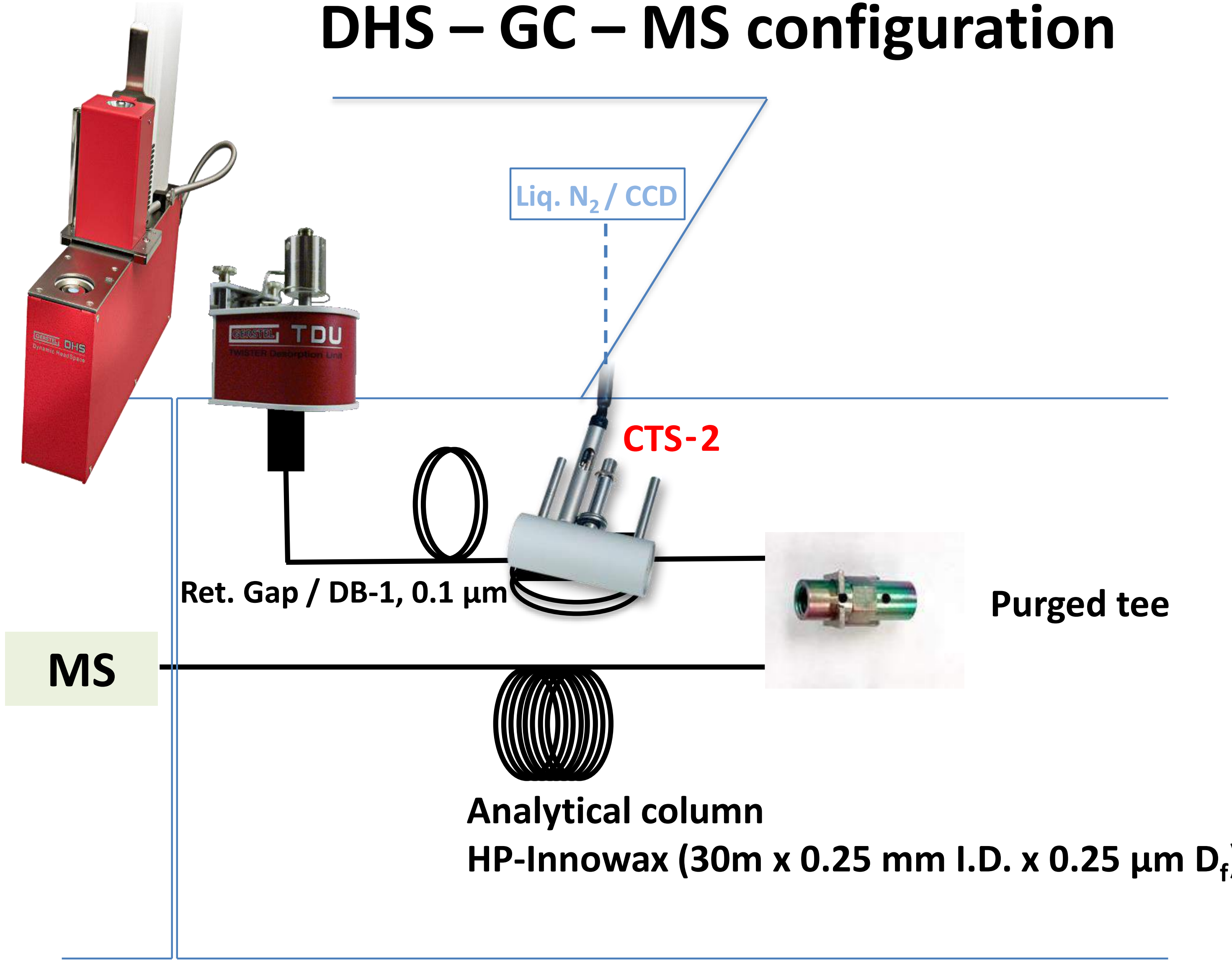
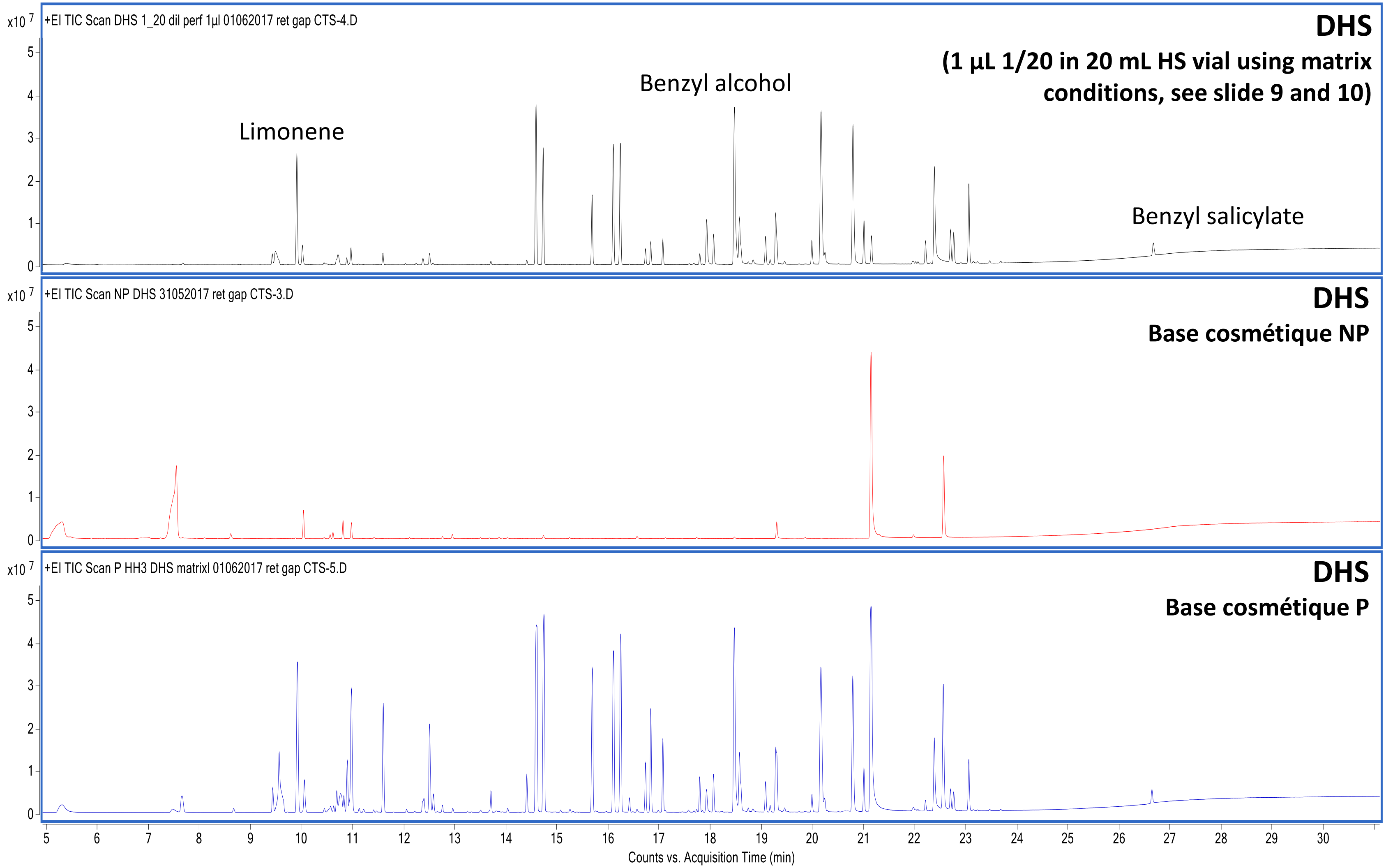
DHS – GC – MS configuration



DHS TDU CTS2
200 mg matrix (base cosmétique) in 20 mL HS vial



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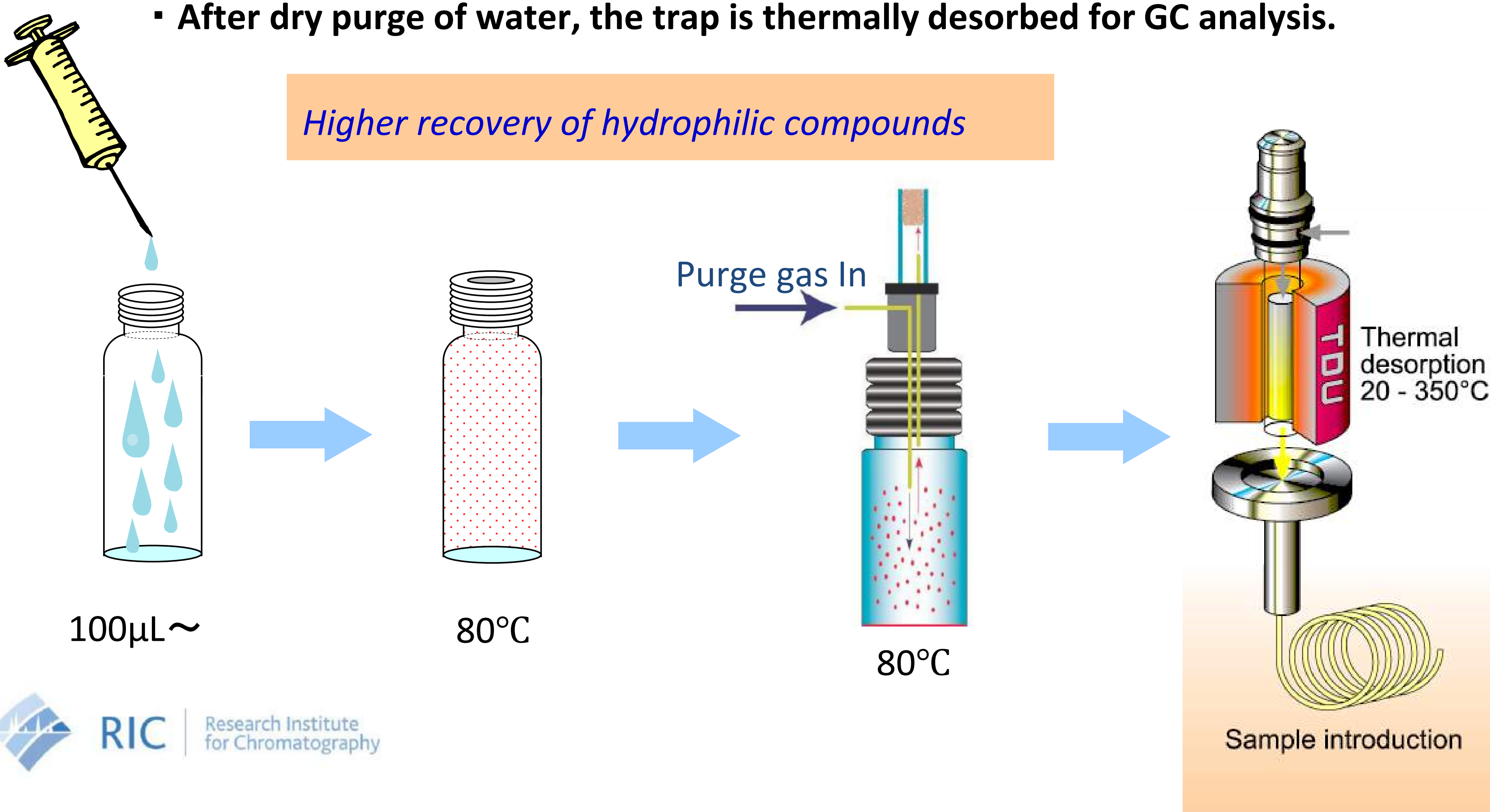
Full evaporation dynamic headspace (FEDHS)

- **100 µL of aqueous sample is dispensed into a HS vial and purged with inert gas at an elevated temperature (80ºC) using DHS.**
- **Volatile and semi-volatile analytes are transferred into the trap (Tenax).**
- **After dry purge of water, the trap is thermally desorbed for GC analysis.**

Higher recovery of hydrophilic compounds



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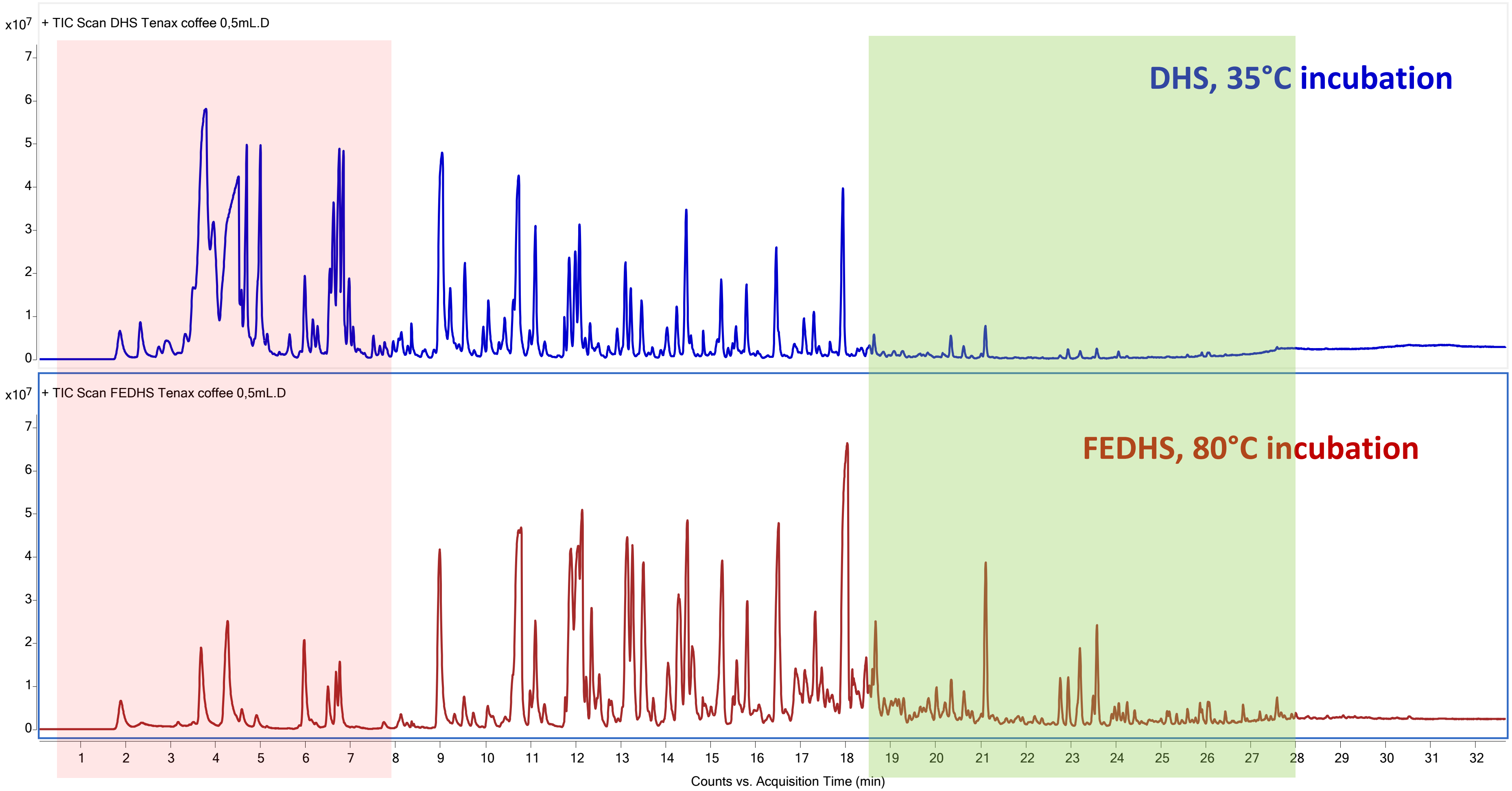
FEDHS method parameters

- *FEDHS conditions*
  - *Sample volume: 50 µL – 100 µL*
  - *Trap:* ***Tenax***
  - ***Trap temperature: 40°C***
  - ***Incubation temperature: 80°C***
  - ***Purge: 2500 mL @ 100 mL/min → dry purge 500 mL @ 100 mL/min***
- *TDU/CIS conditions*
  - *TDU: 30°C, 60°C/min to 270°C (5 min)*
  - *Transfer temperature: 280°C (splitless)*
  - *CIS: -100°C, 12°C/sec to 280°C (7 min) using a Tenax liner*

Classical DHS vs FEDHS - GC-MS of coffee



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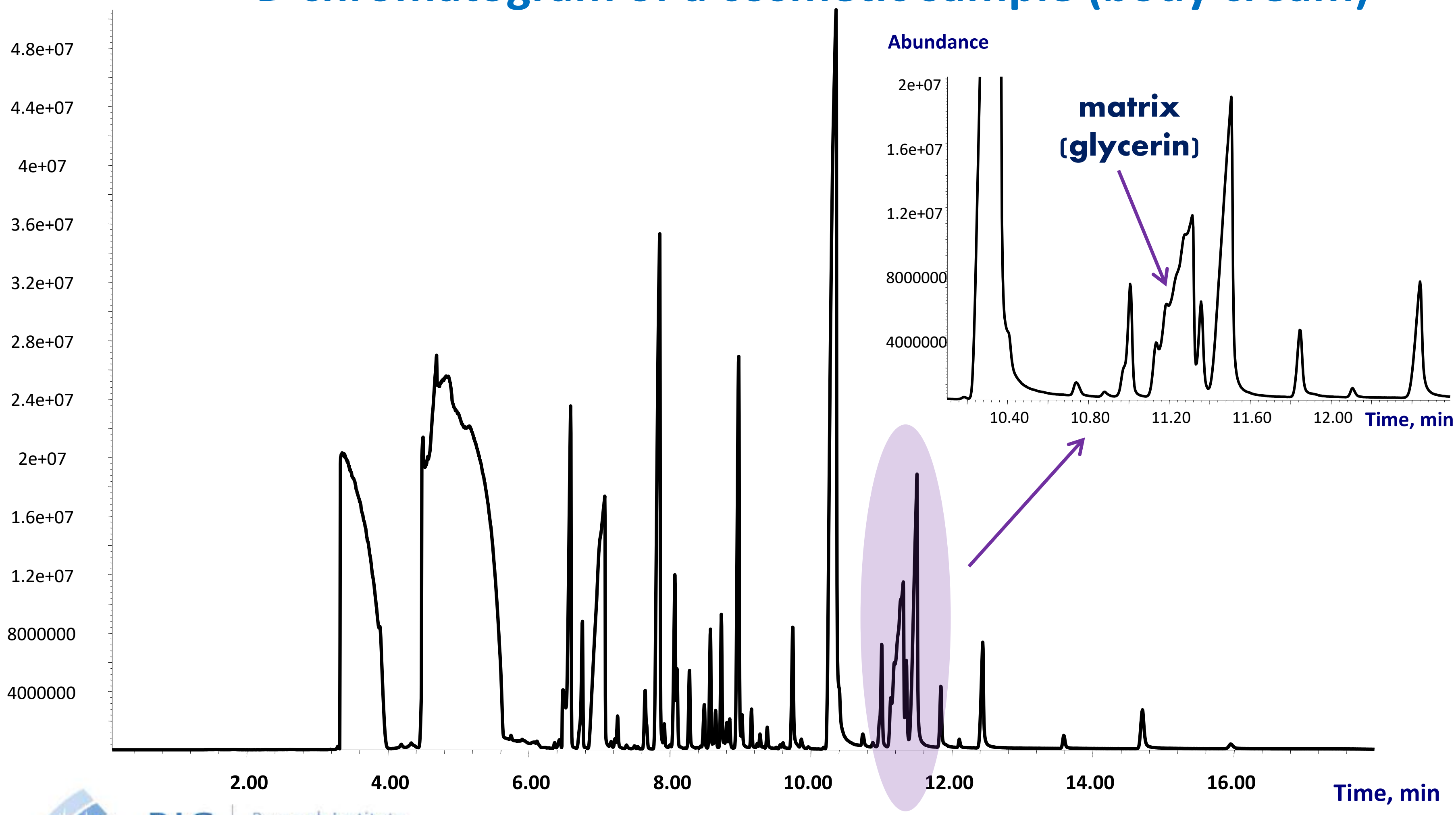
Selectable ^{1}D/^{2}D analysis of allergens in cosmetics in combination with FEDHS

^{1}D chromatogram of a cosmetic sample (body cream)



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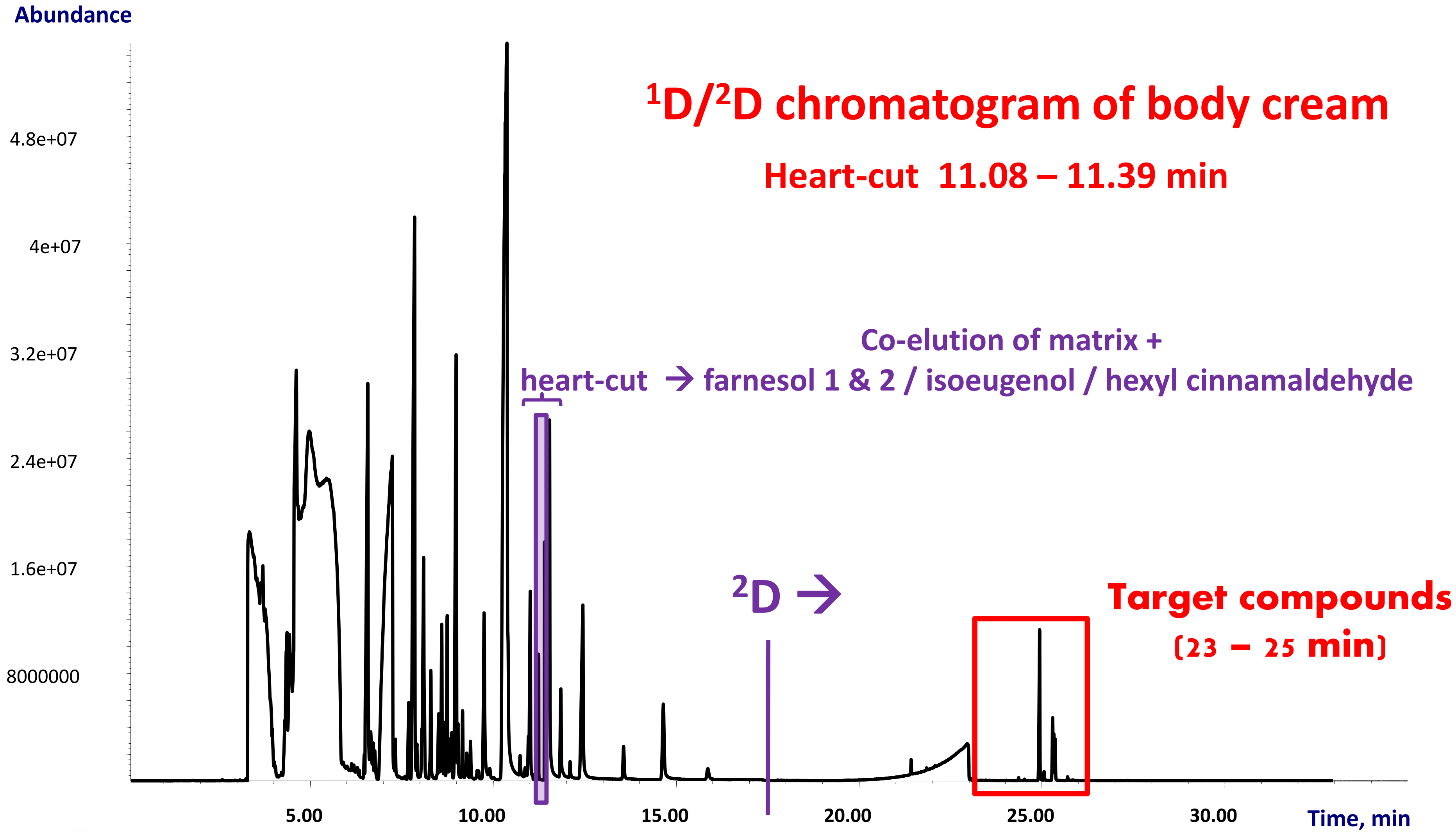
Selectable $^{1}D/^{2}D$ analysis of allergens in cosmetics in combination with FEDHS



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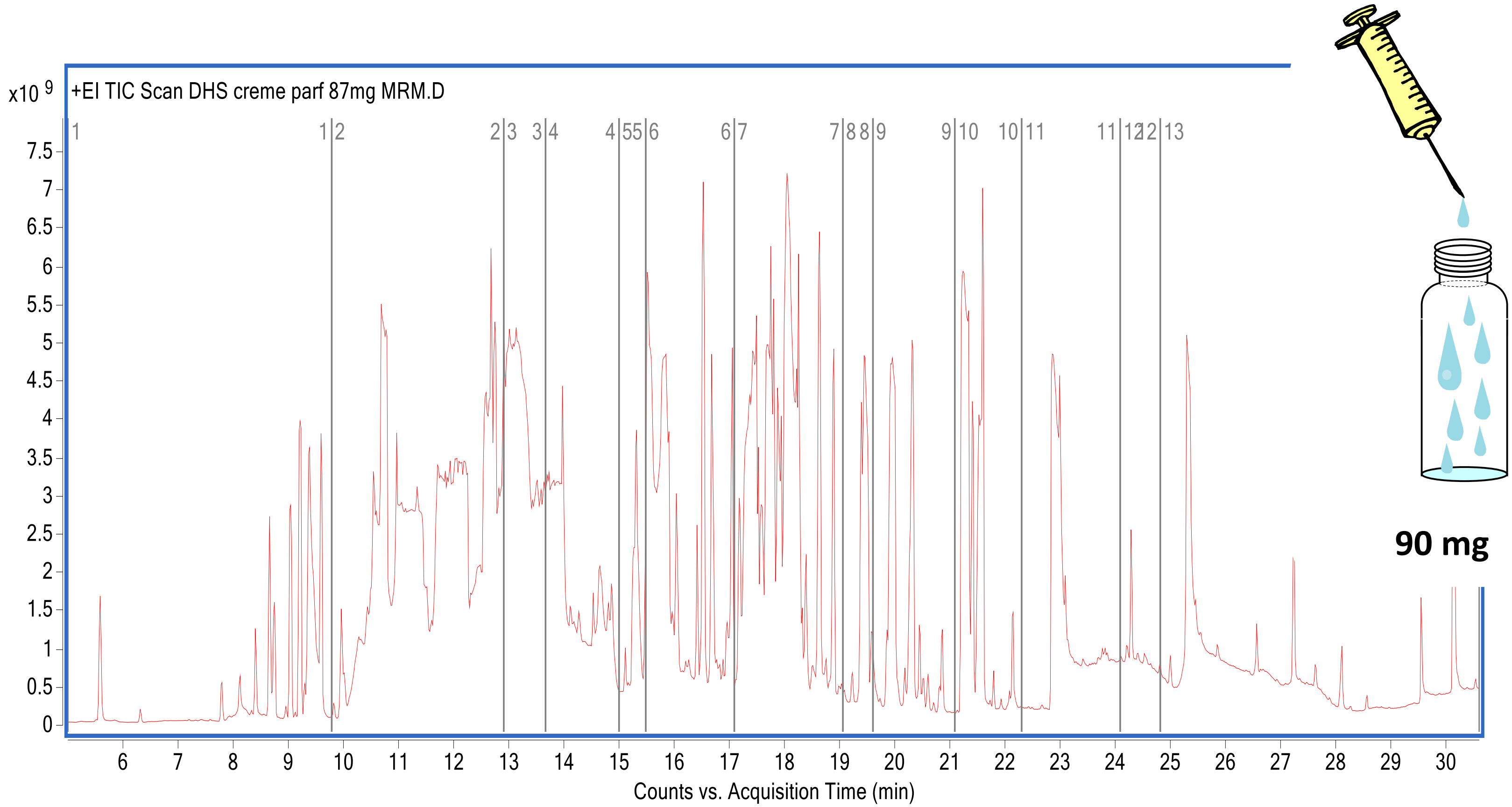
Allergen profile Crème parfumée – Pure Sample/Matrix in DHS

FEDHS at 80 C (3000 mL purge volume) – 90 mg sample in 20 ml vial
Scan chromatogram – Overloaded (Matrix components)!



90 mg

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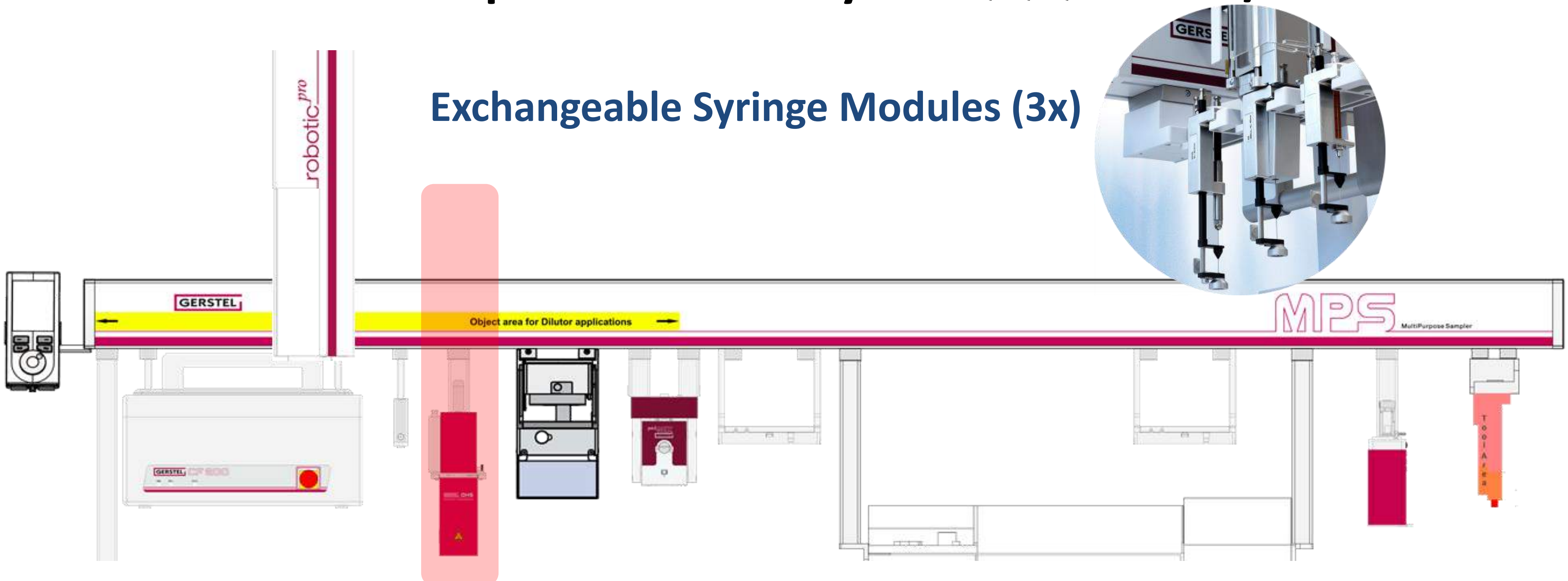
Further DHS automation: Extraction of allergen compounds from cosmetic samples followed by GC QQQ in Scan/MRM



Automated Sample Preparation:

Add extraction solvent (SFS-3 solvent station)

Extraction/Dilution (strong Quickmix agitation)

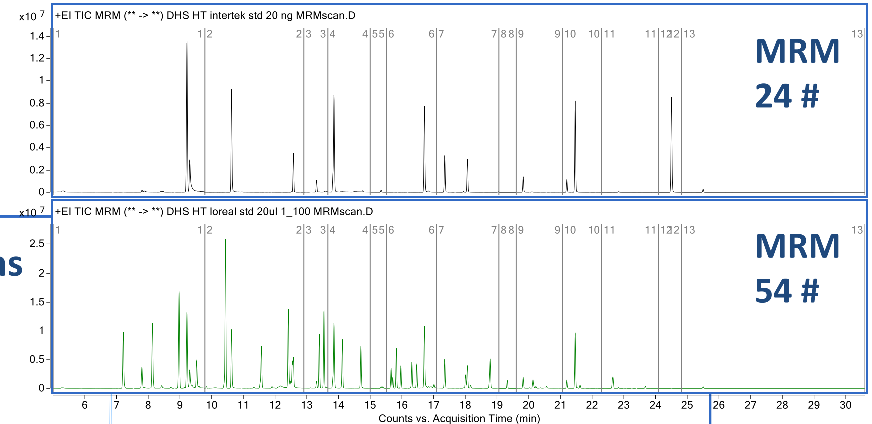
Centrifuge (CF200)

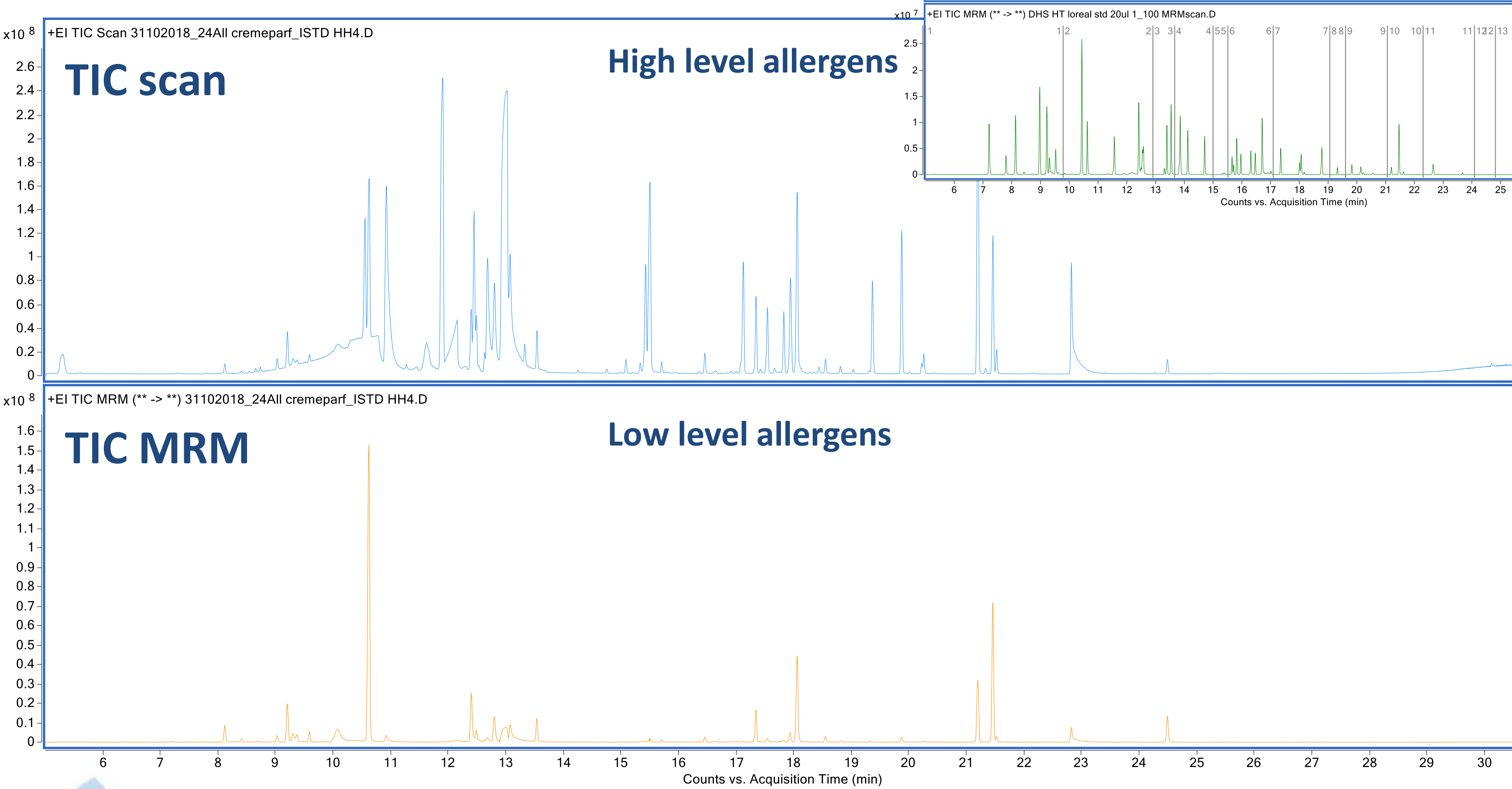
De-cap 20 ml HS vial / Transfer 20 µL / add ISTD / re-cap (automated capper/re-capper)

FEDHS enrichment – GC – QQQ (scan/MRM)

Allergen profile Crème parfumée: scan/MRM

Modified method: 100 mg sample / 1 mL acetone → 20 µL of extract in 20 mL HS vial → FEDHS





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Allergen profile Crème parfumée: MH batch Quantification

Crème parfumée

Agilent MassHunter Quantitative Analysis (for QQQ) - final quant DHS MRM - MH QuantMR . arf.batch.bin

File Edit View Analyze Method Update Library Report Tools Help

Analyze Batch · Layout: · Restore Default Layout

Batch Table

Sample: ORe18162 100pp... · Sample Type: <All> · Compound: Linalol · ISTD: ISDT 1 (1,4 dibromo

Compound Method		ORe18162 100ppm monste...		ISTD Re...	ORe18162 100ppm monste...		ISTD Re...
Name	Transition	RT	Final Conc.	Area	RT	Final Conc.	Area
Benzyl alcohol	79.0 -> 77.0	9.315	14.3444	11553510	9.305	100.0000	10726244
Linalol	93.0 -> 77.0	10.627	467.9566	11553510	10.634	100.0000	10726244
Folione (Me-2-octynoate)	123.0 -> 93.0	12.488		11553510	12.579	100.0000	10726244
Citronellol	95.0 -> 55.0	13.002	302.9998	11553510	13.008	100.0000	10726244
Neral	94.0 -> 79.0	13.089		11553510	13.321	100.0000	10726244
Geraniol	93.0 -> 77.0	13.576	10.3978	11553510	13.593	100.0000	10726244
Citral	94.0 -> 79.0	13.541		11553510	13.831	100.0000	10726244
Cinnamaldehyde	131.0 -> 77.0	13.864	0.0625	11553510	13.864	100.0000	10726244
Anisyl alchol	138.0 -> 109.0	14.100	0.1068	11553510	14.077	100.0000	10726244
Hydroxycitronellal	96.0 -> 81.0	14.091	0.0751	11553510	14.097	100.0000	10726244
Cinnamyl alcohol	134.0 -> 92.0	14.511	0.0905	11553510	14.471	100.0000	10726244

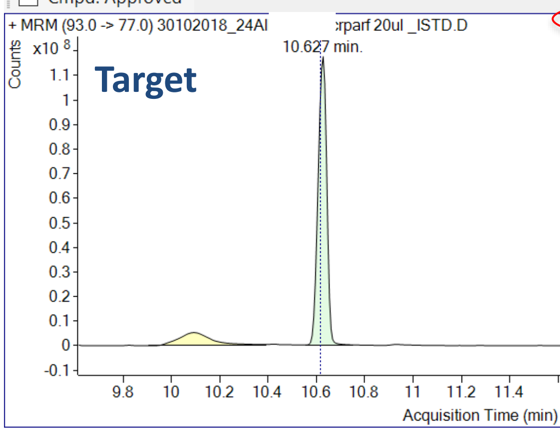
← **Linalol**

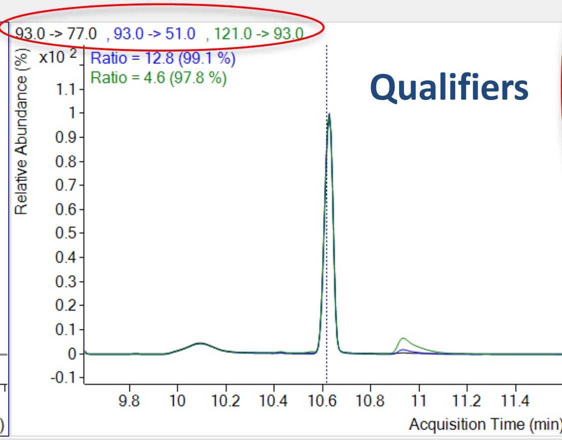
Retention Time Locking (RTL)
Dynamic MRM-mode

Compound Information

Minutes

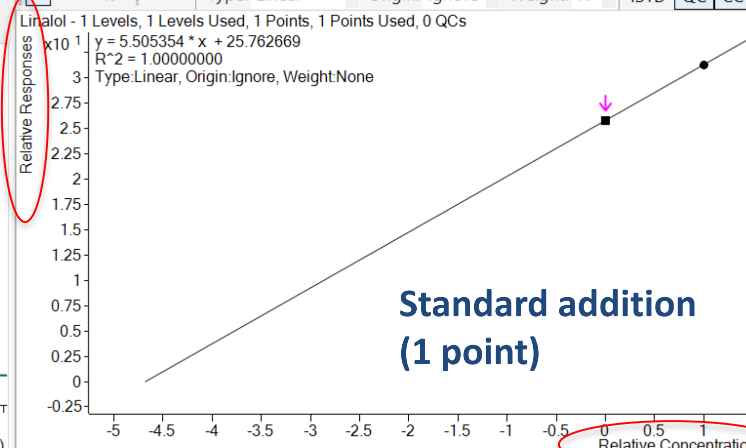
Cmpd. Approved





Calibration Curve

Type: Linear · Origin: Ignore · Weight: N · ISTD QC CC



Processed | ORe18162 100ppm monster conc | Linalol | 26 Compounds (28 total including ISTDs) | RIC\christophed

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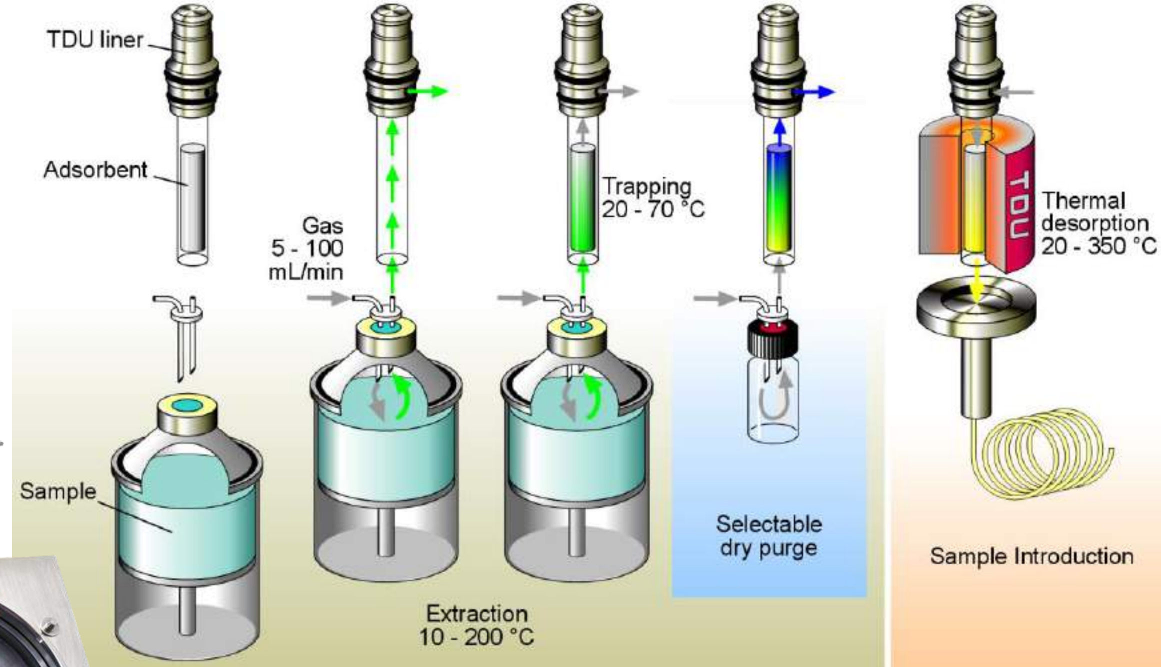
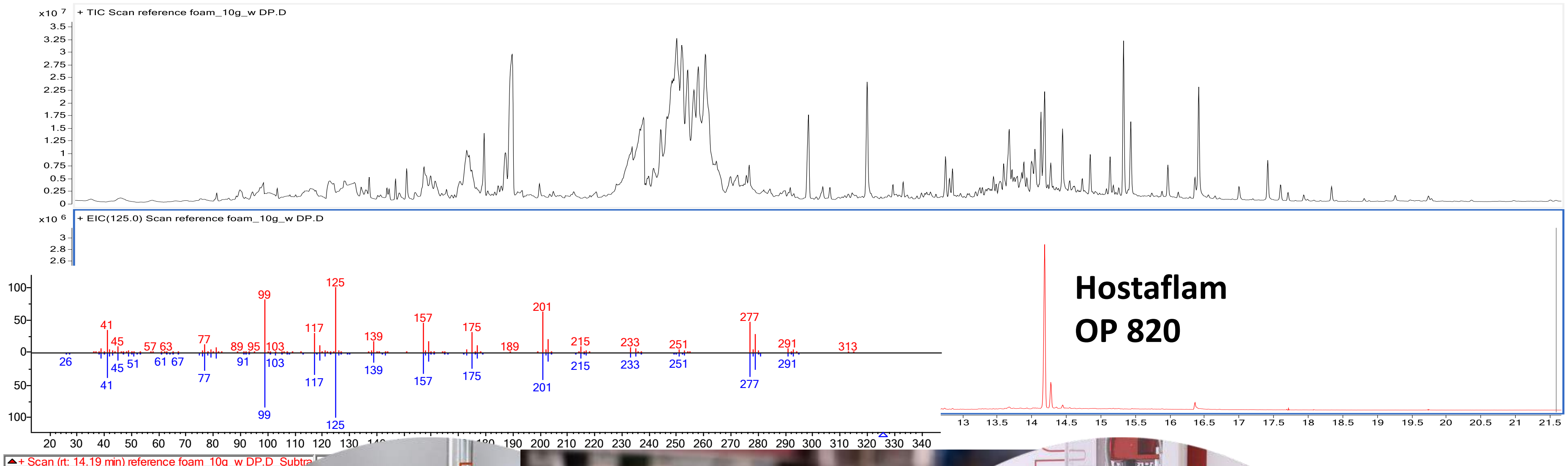
DHS Large – More material – Material Emission



DHS 3.5+ – DHS / DHS Large – More Capacity / Homogeneity



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Volatiles in chemical analysis:

1. Static headspace (SHS) – (CTS 2 refocusing)
2. **HS**-SPME (headspace)
3. Dynamic Headspace (DHS) – (CTS 2 refocusing)
4. Multi Volatile Method (MVM) - DHS
5. Full evaporation DHS (FEDHS)

   FEDHS is the only DHS mode that has the potential to provide profiles identical to liquid injection.

6. Sample Prep Automation SE-DHS
7. DHS large and DHS for TD3.5+

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