

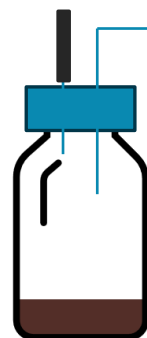
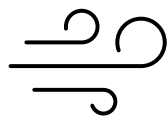
Empower headspace extraction exploiting novel, automated sample concentration techniques

Damien Eggermont

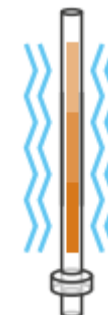


Dynamic vs Equilibrium technics

Dynamic:

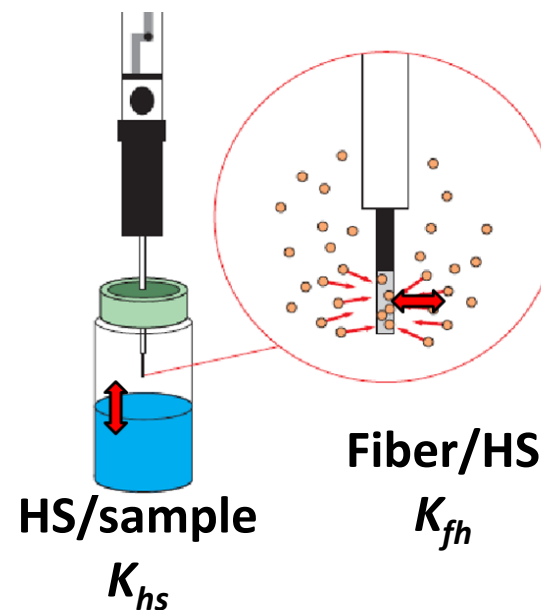
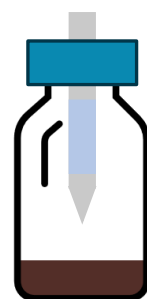


Focussing required



SPME

Equilibrium:



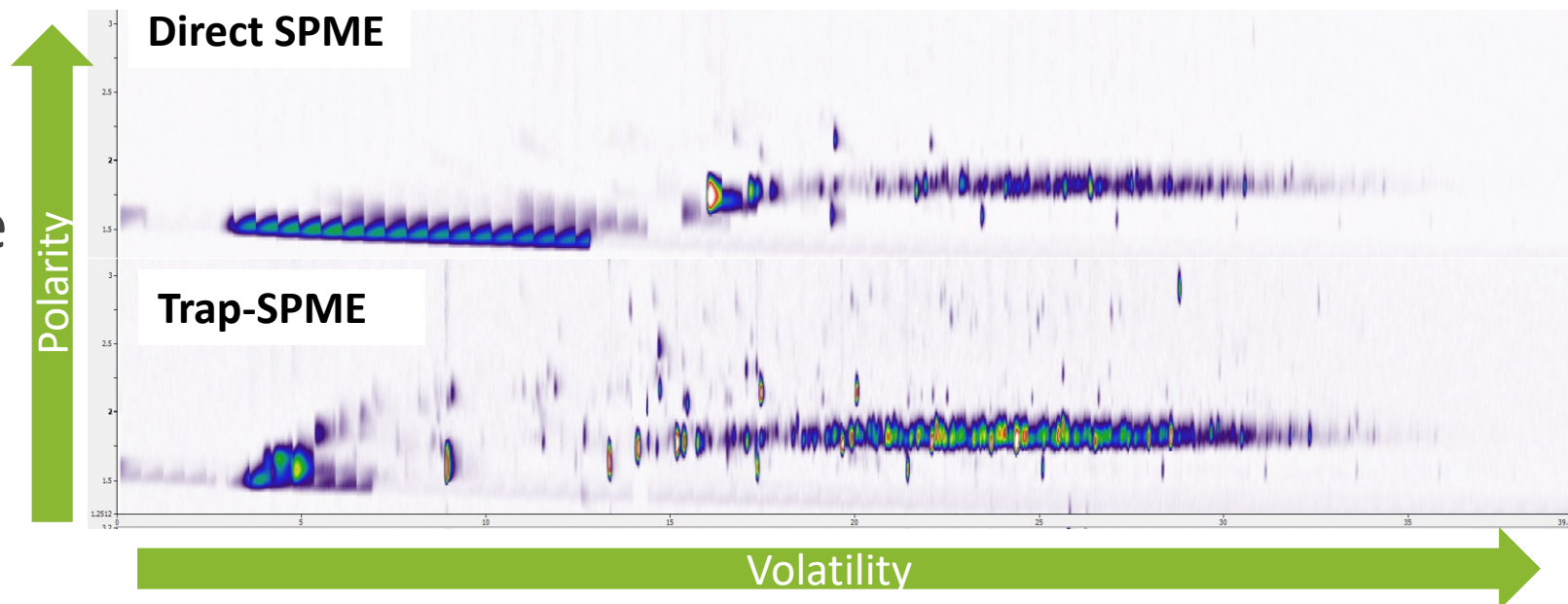
Focussing on the tool

Depending on the tool

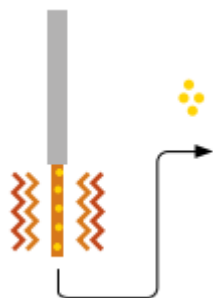


Desorption optimisation

- Temperature
- Time
- (Flow)



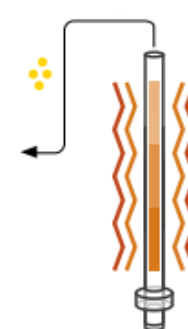
Direct SPME :



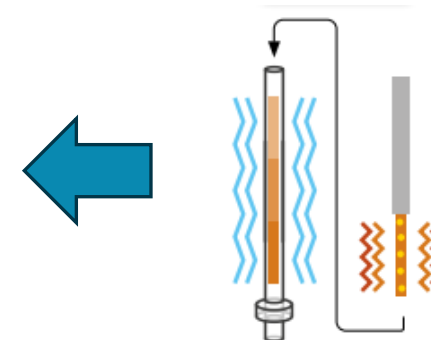
Desorption & injection



Separation & Detection



2) Injection



1) Desorption & focussing

: Trap-SPME

Different tools for different selectivity

Fiber



Arrow



HiSorb



Thin-Film



V_{sorbent} :

~0.6 μL

~3.8-12 μL

~67 μL

~60 μL

Surface:

~9.4 mm^2

~44-63 mm^2

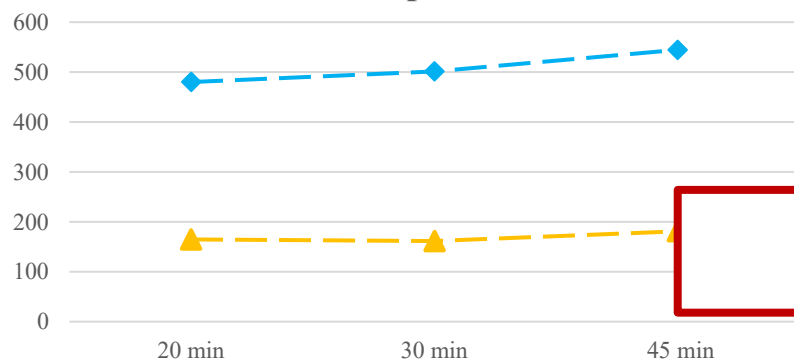
~65 mm^2

~190-200 mm^2

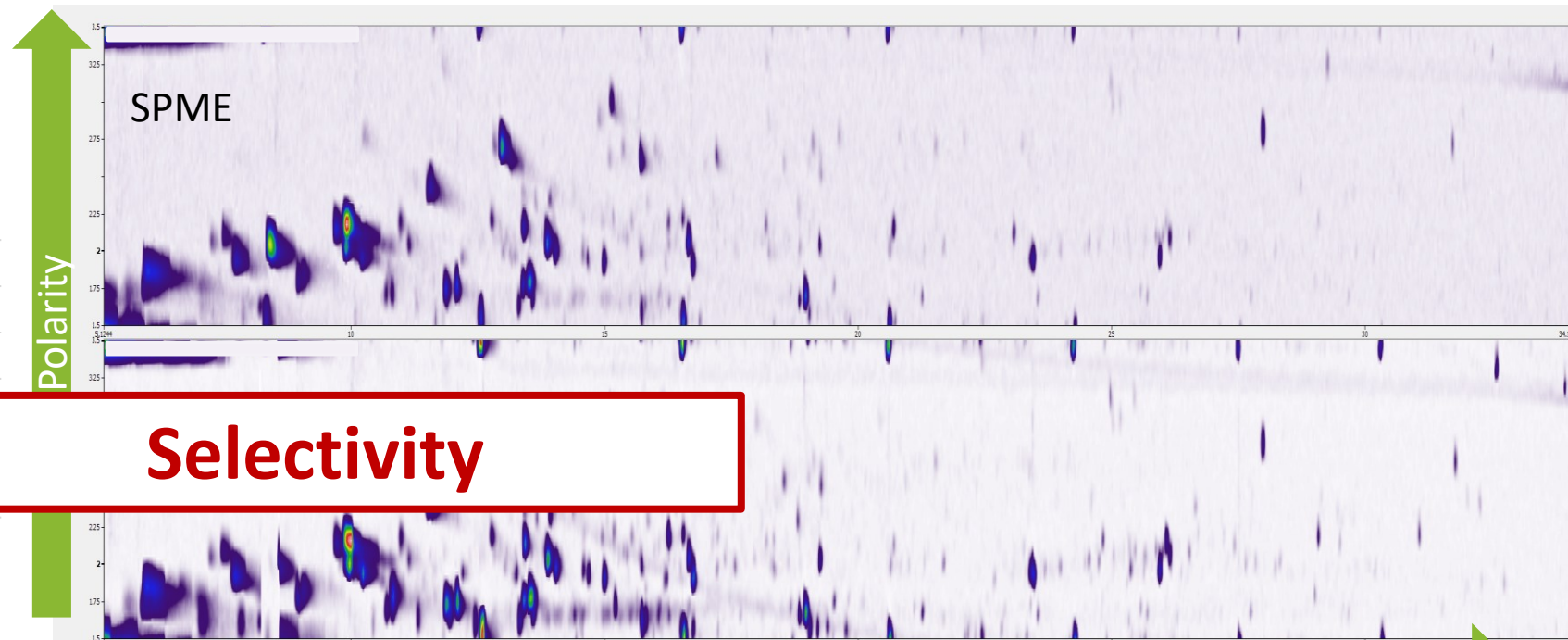
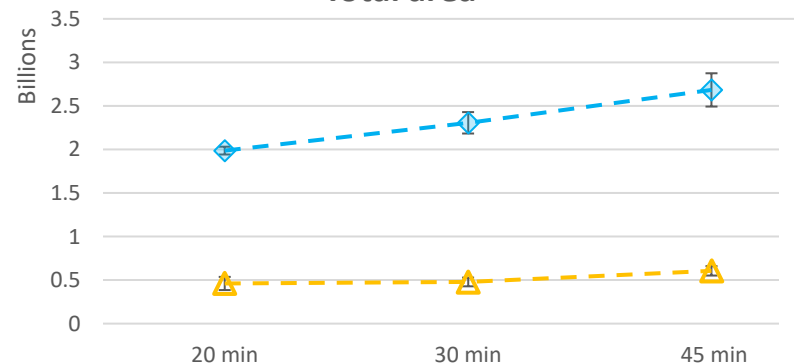
Comparison Fiber/HiSorb

—●— HS-Hisorb (CWR/DVB/PDMS)
—△— HS-SPME (CAR/DVB/PDMS)

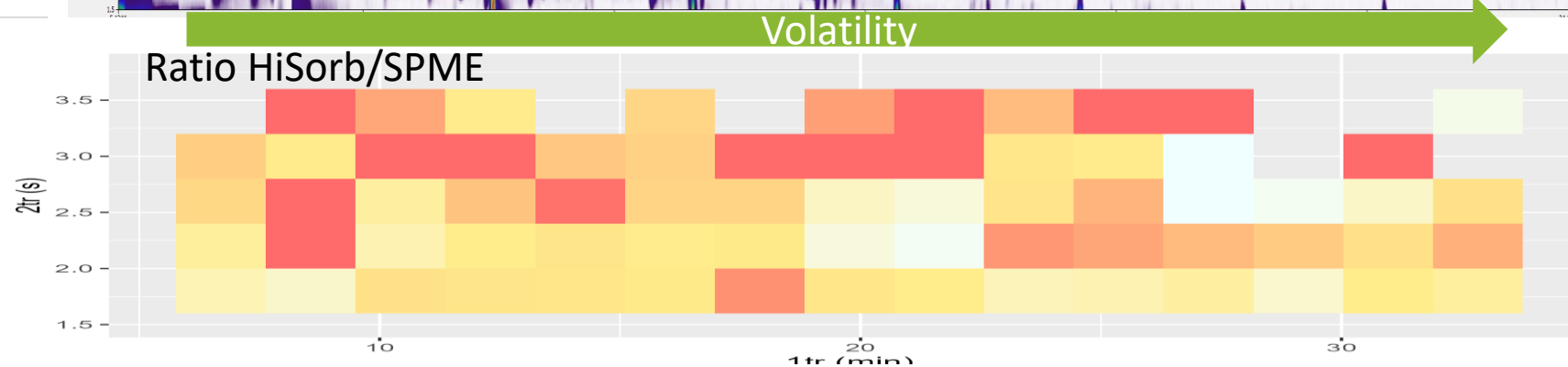
N° of peak



Total area



Selectivity



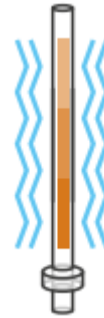
Different mode of HS extraction

- Pressure



- Number of cumulated extraction

- Same vial
- Multiple vials



Different mode of HS extraction

- Pressure



- Number of cumulated extraction

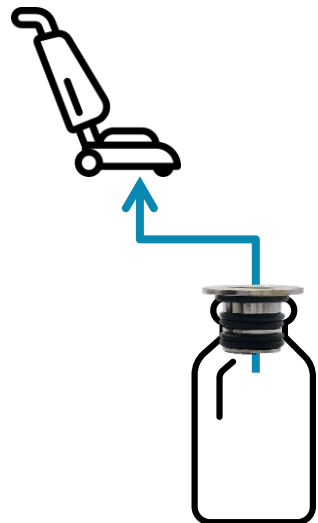
- Same vial
- Multiple vials



Playing with pressure: Vac-HS-SPME



Procedure: Liquid samples



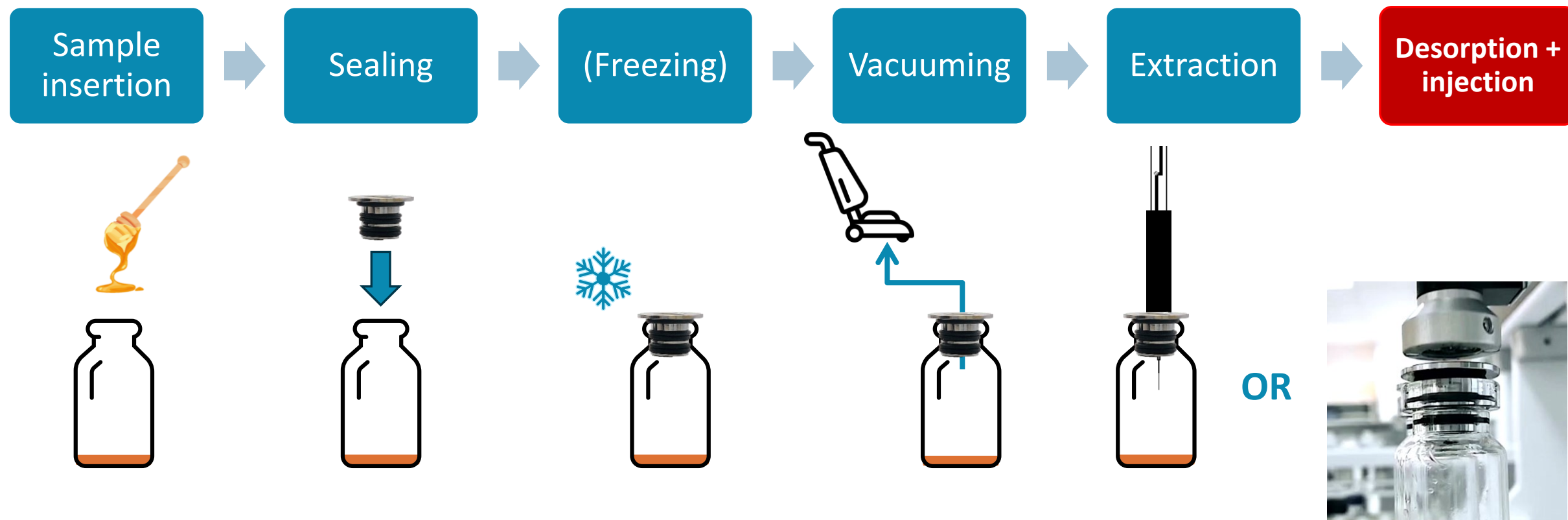
OR



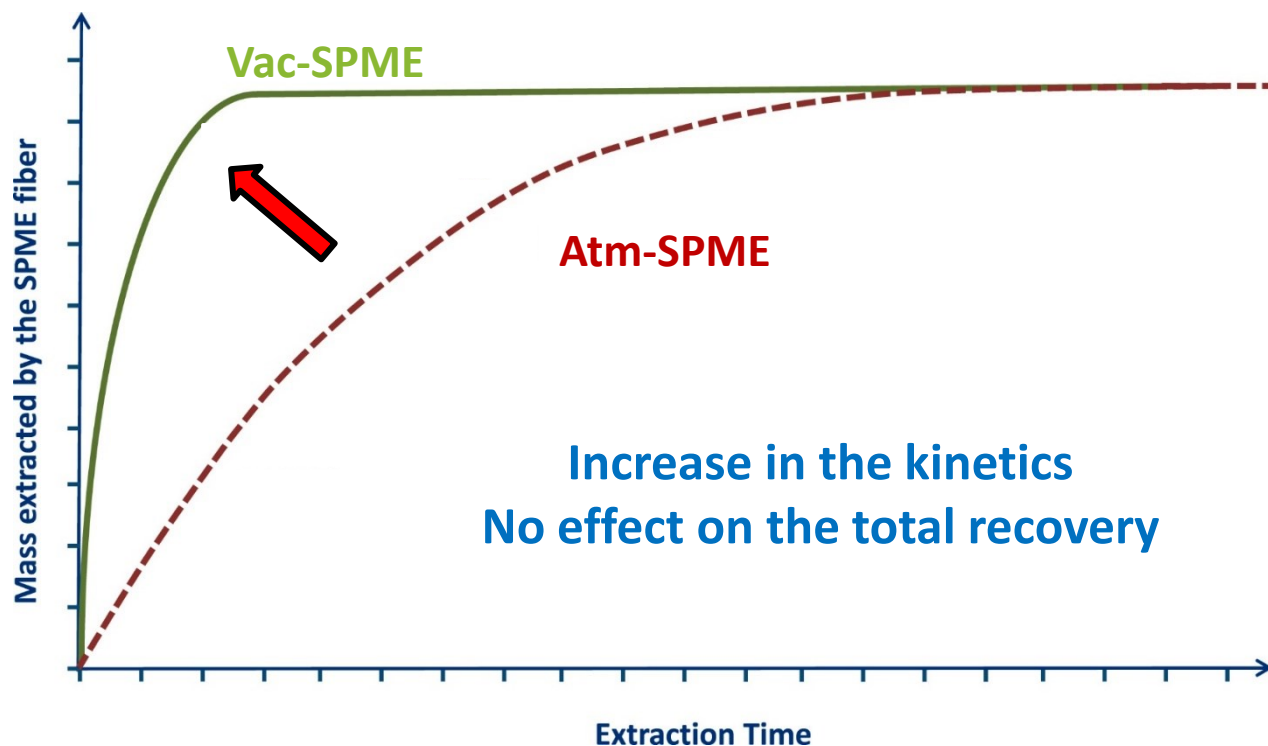
Playing with pressure: Vac-HS-SPME



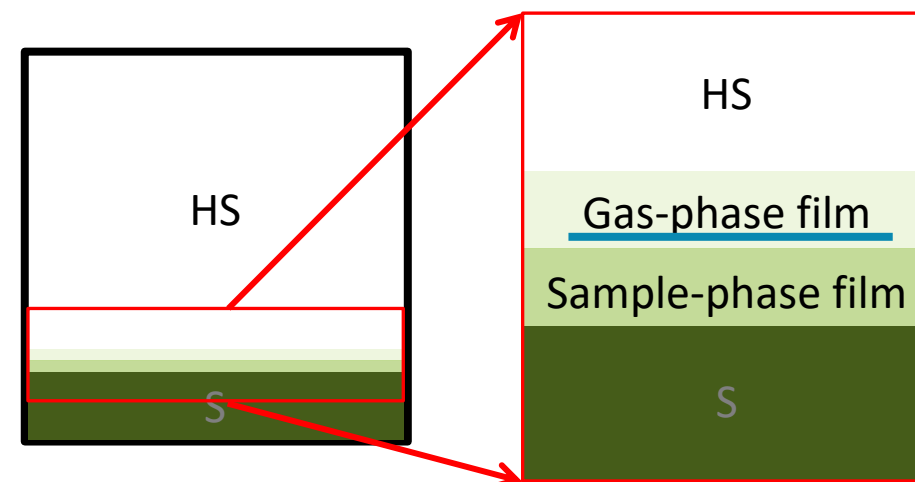
Procedure: Liquid and solid samples



Playing with pressure: Vac-HS-SPME

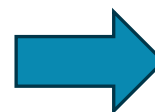


Two boundary layer model :



Vac: resistance decrease in gas-phase film

**Volatiles equilibrate faster than
SVOCs**

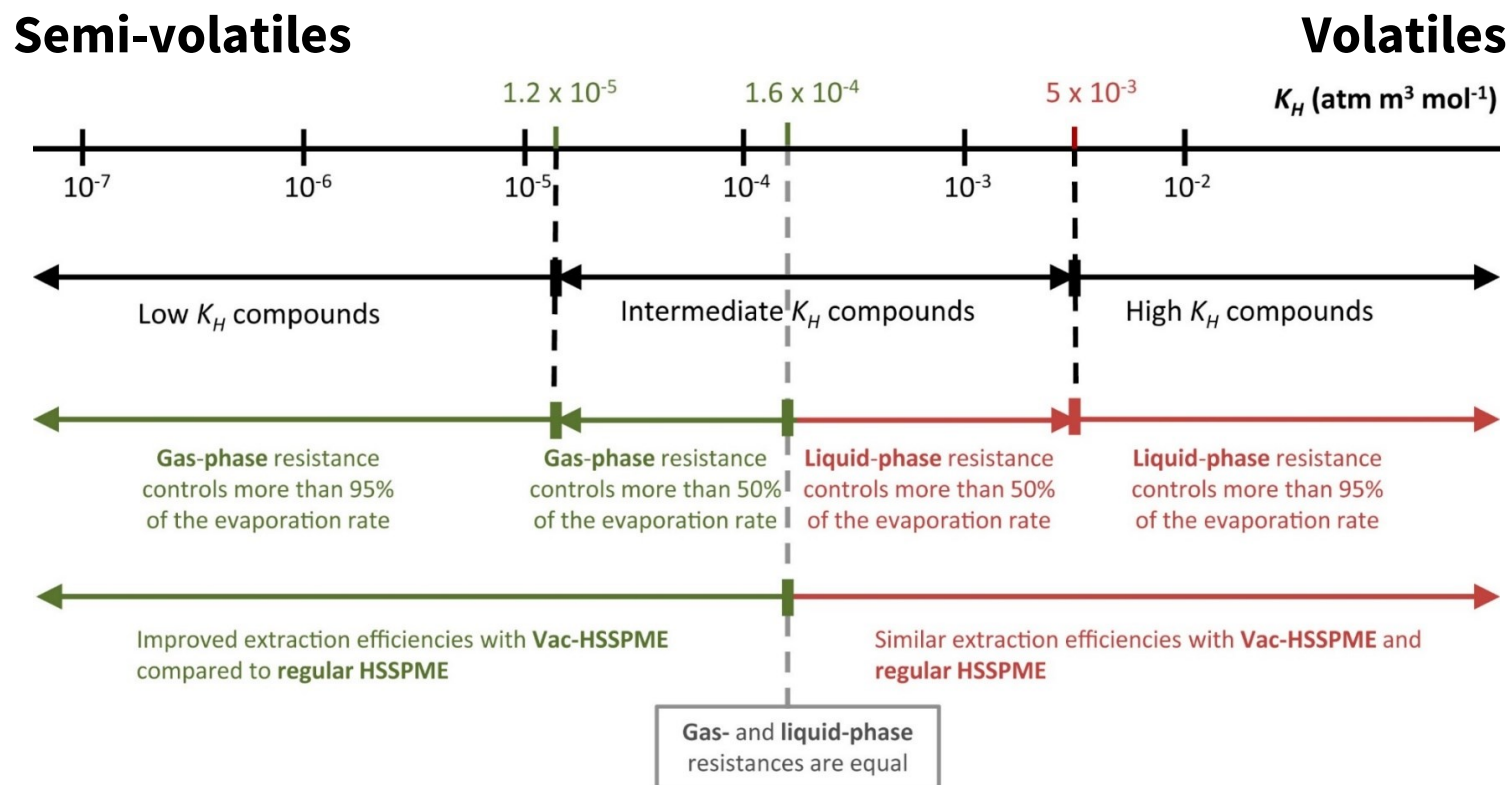


Vac speeds SVOCs equilibration

Playing with pressure: Vac-HS-SPME



Criterion to predict the effect of vacuum : K_H



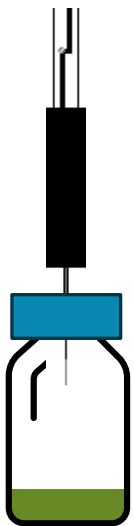
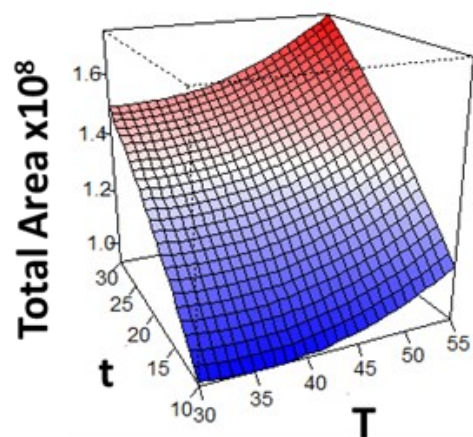
Water-based samples

Playing with pressure: Vac-HS-SPME

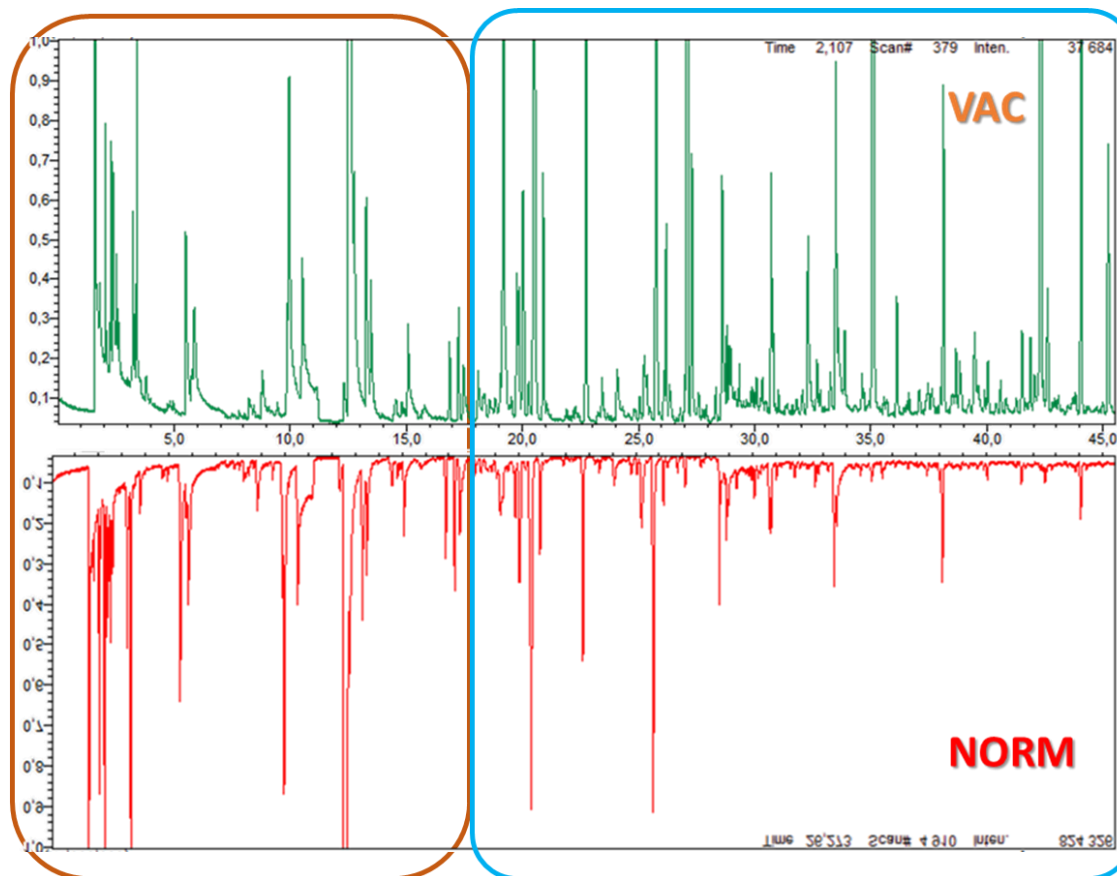
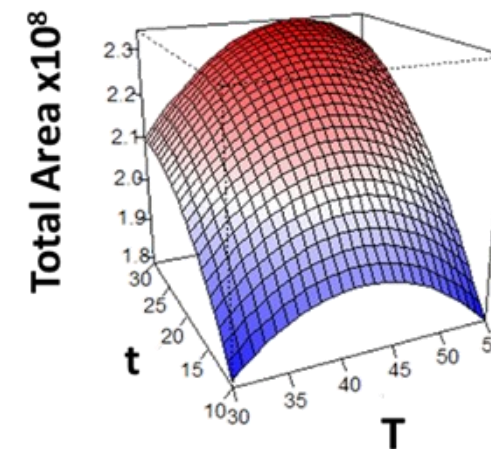


Olive oil analysis

Atm-HS-SPME



VAC-HS-SPME



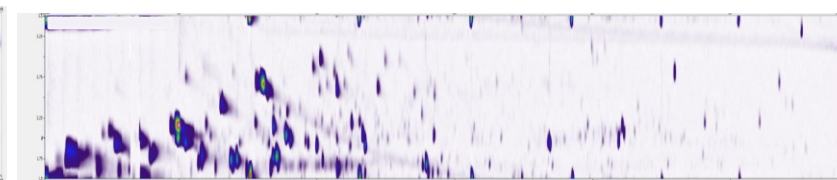
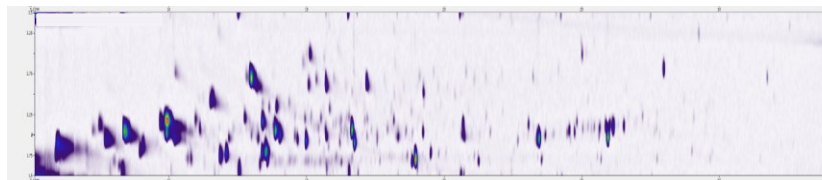
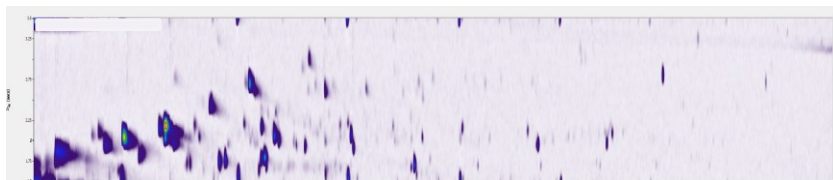
Playing with pressure: Vac-HS-SPME



Atm-HS-SPME

Vac-HS-SPME

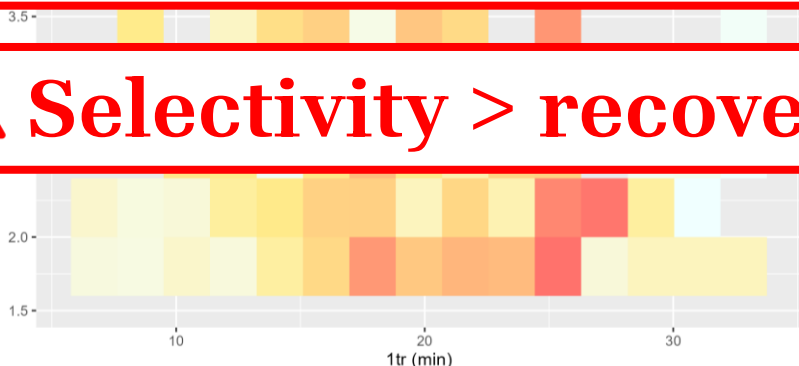
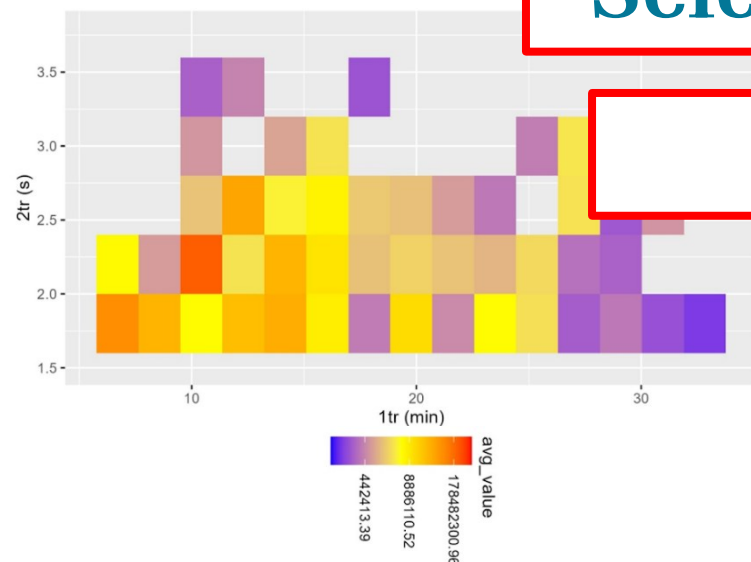
HiSorb®



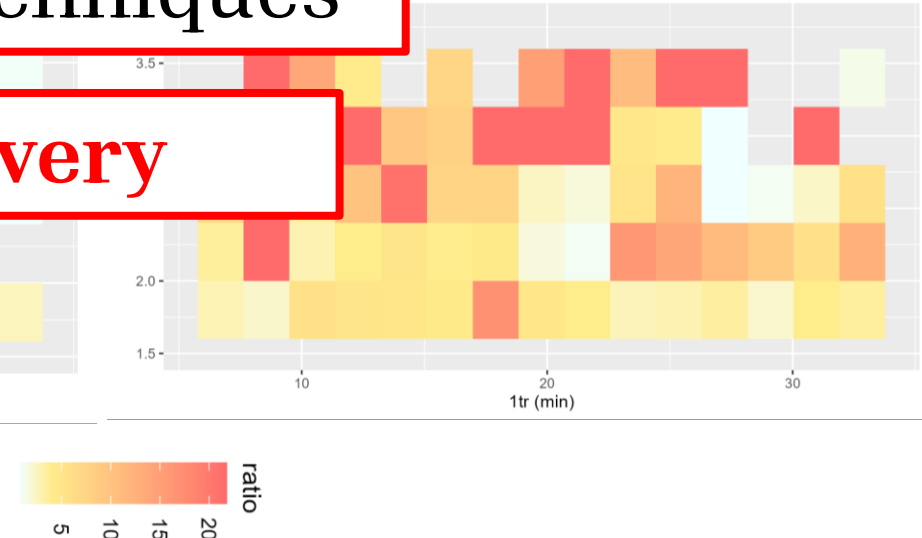
Selectivity of different techniques

⚠ Selectivity > recovery

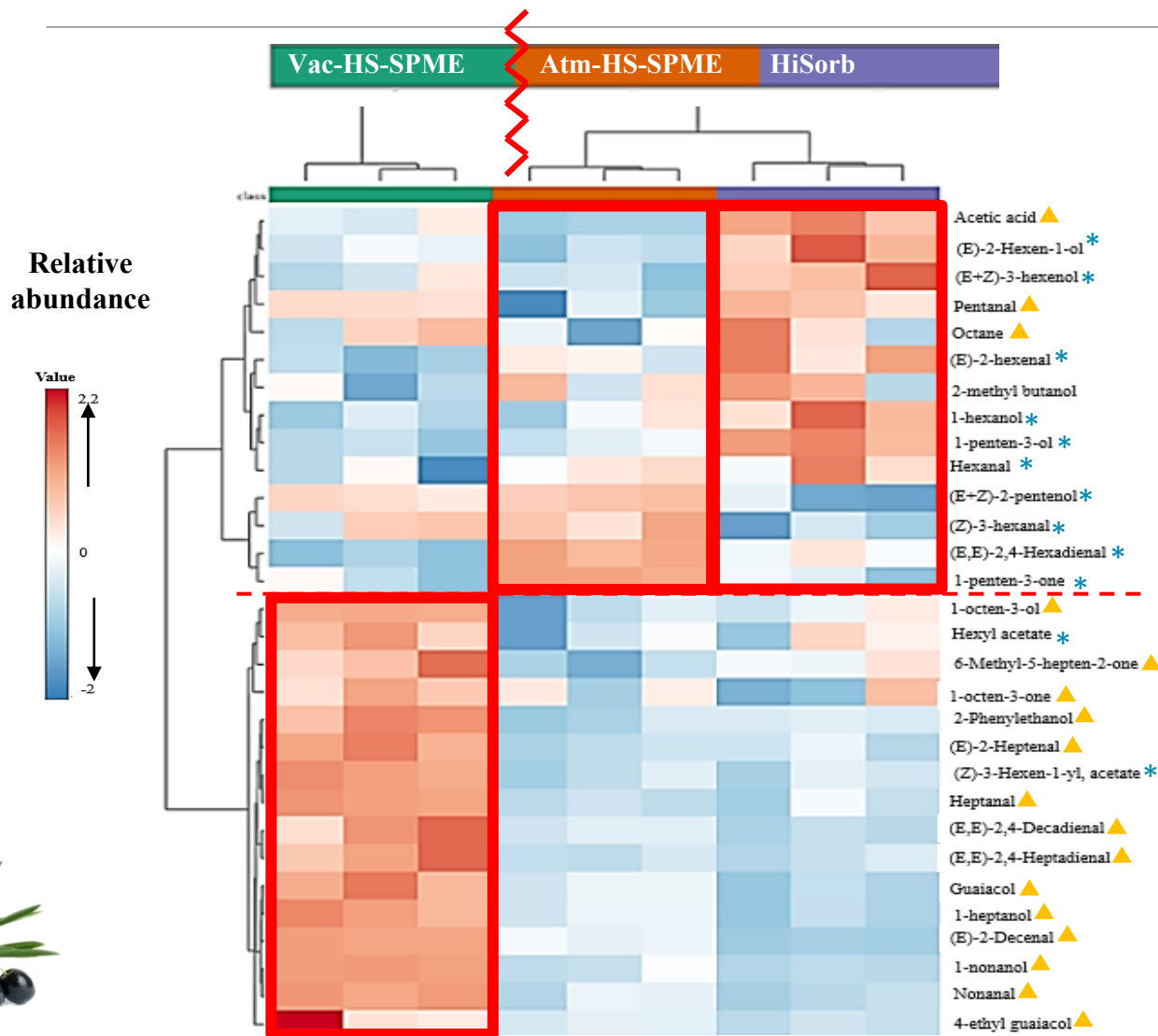
Area



HiSorb/HS-SPME

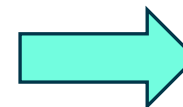


Playing with pressure: Vac-HS-SPME



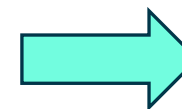
Selectivity of different techniques

Higher
volatility



**Lipoxygenase
Pathway** * (LOX)

Lower
volatility



**Oxidative,
Microbiological defect** ▲



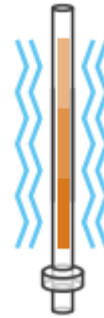
Different mode of HS extraction

- Pressure

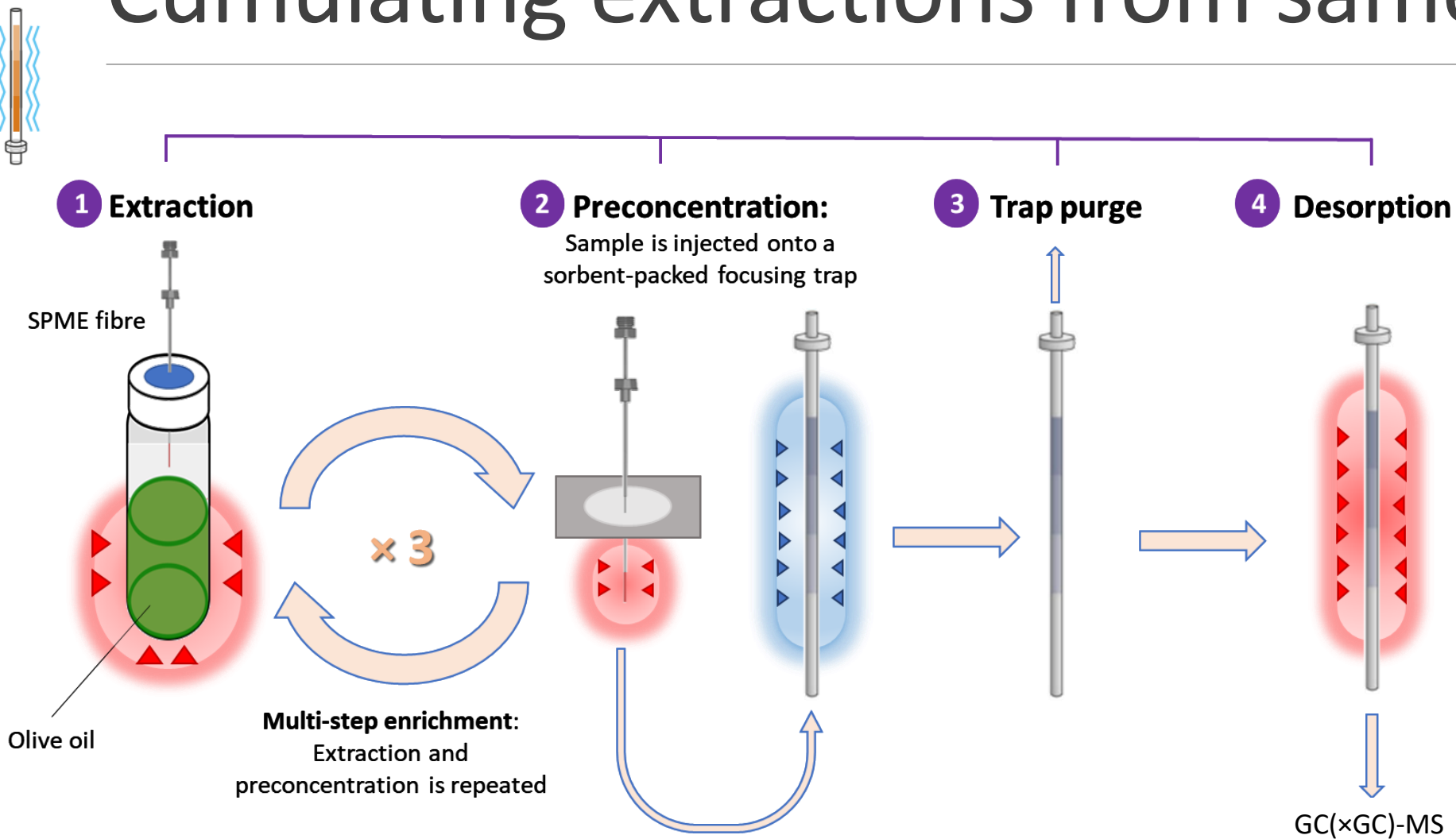


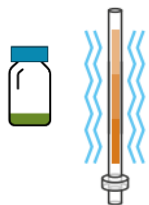
- Number of cumulated extraction

- Same vial
- Multiple vials



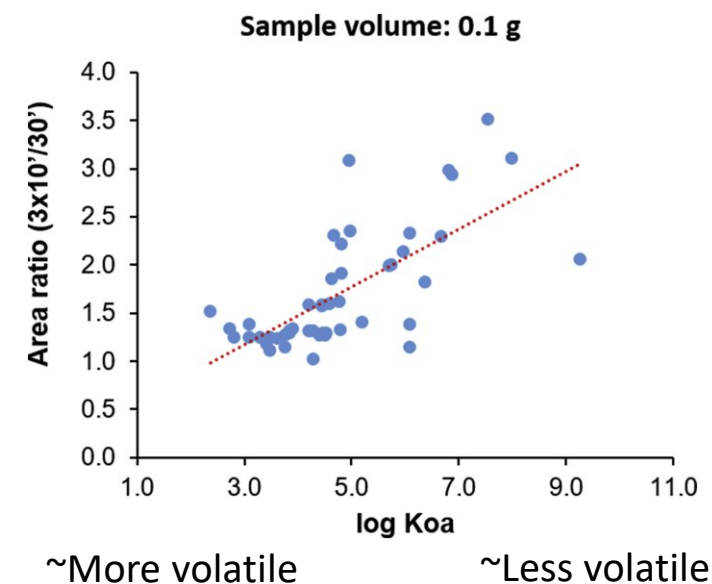
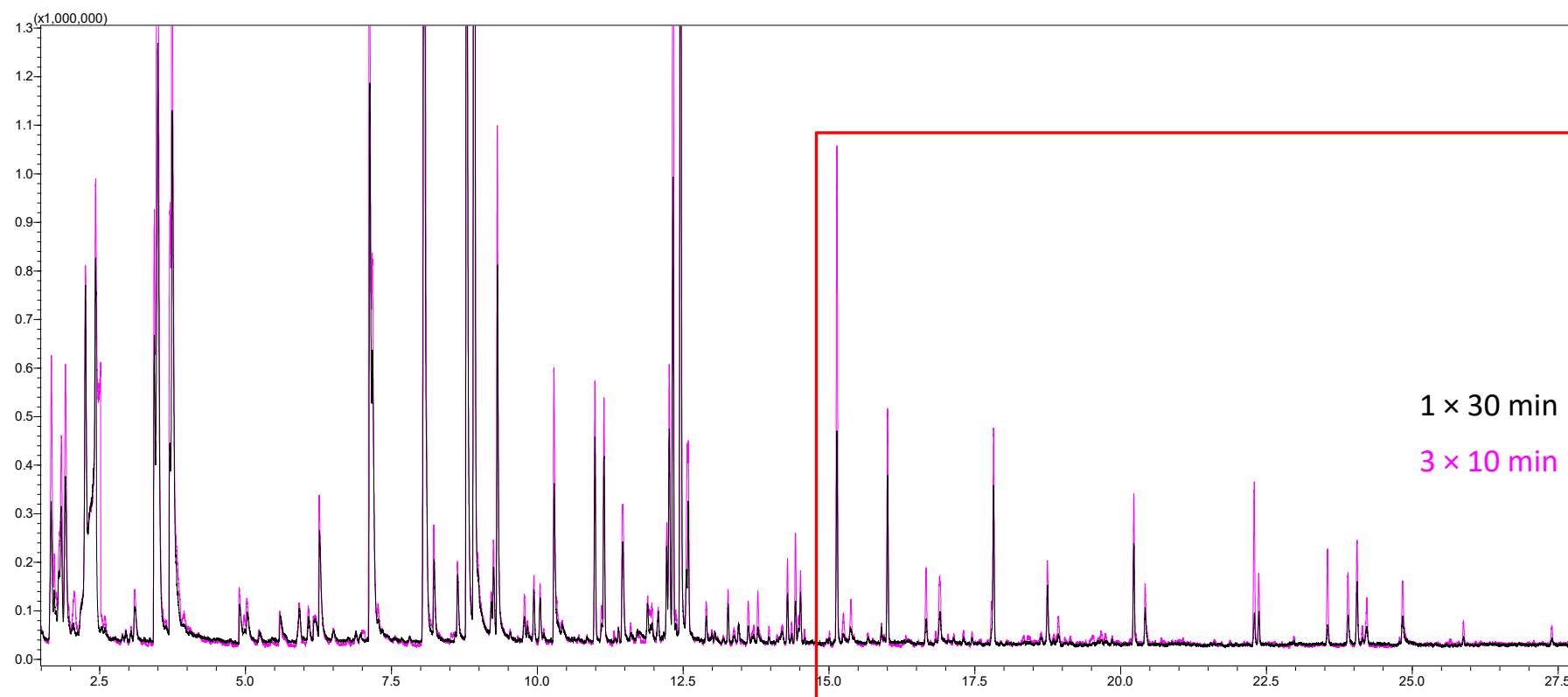
Cumulating extractions from same vial

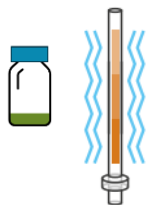




Cumulating extractions from same vial

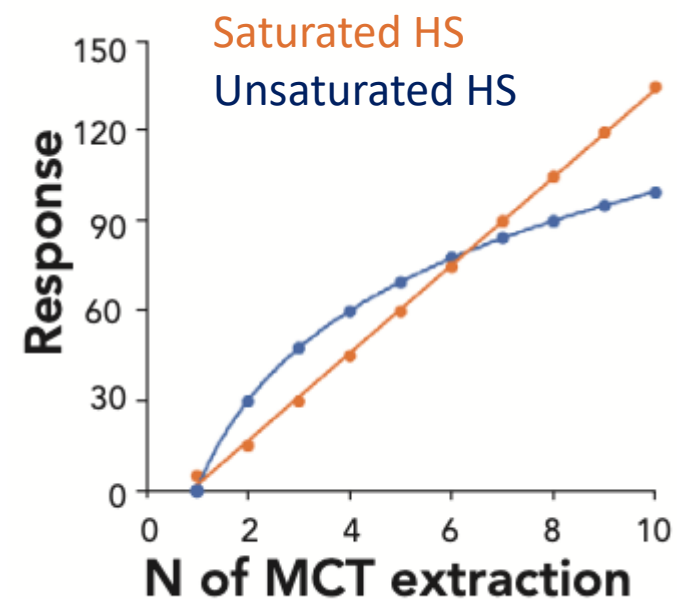
Olive oil analysis





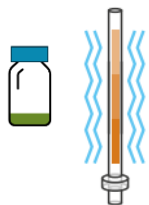
Cumulating extractions from same vial

- Repeated extractions → depletion of HS
- Reduce displacement effect
- Shift toward low VOCs
- Importance of unsaturated HS
 - For broad range of VOC extraction



Depend on the question

Fit for purpose ?

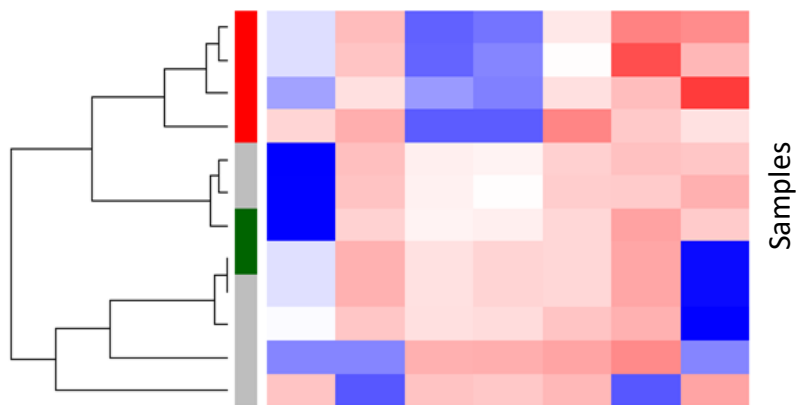


Cumulating extractions from same vial

N of cumulated extractions

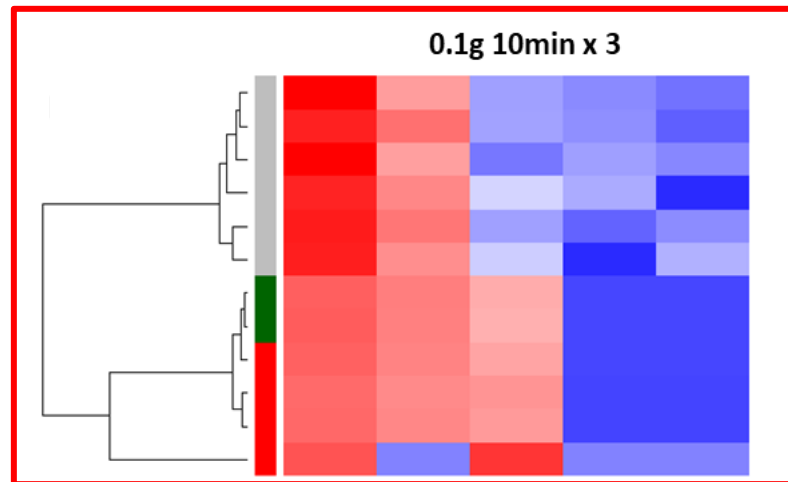


0.1g 10min x 1

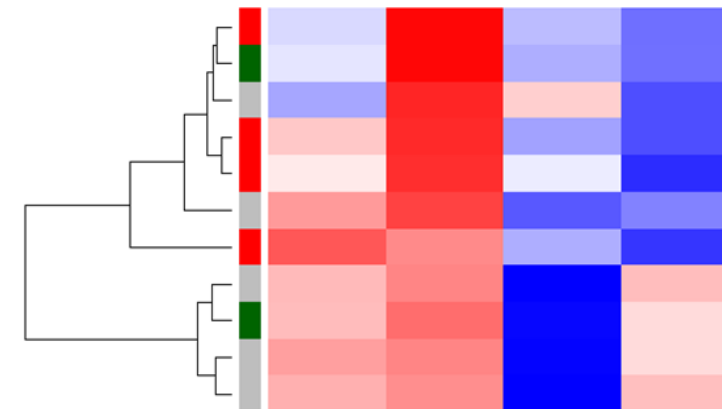


Selected VOCs

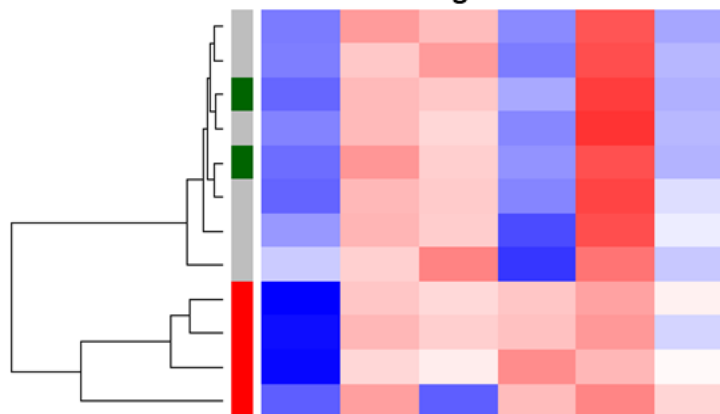
0.1g 10min x 3



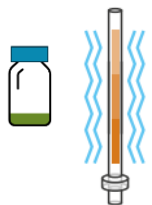
0.1g 10min x 6



0.1g 30min x 1



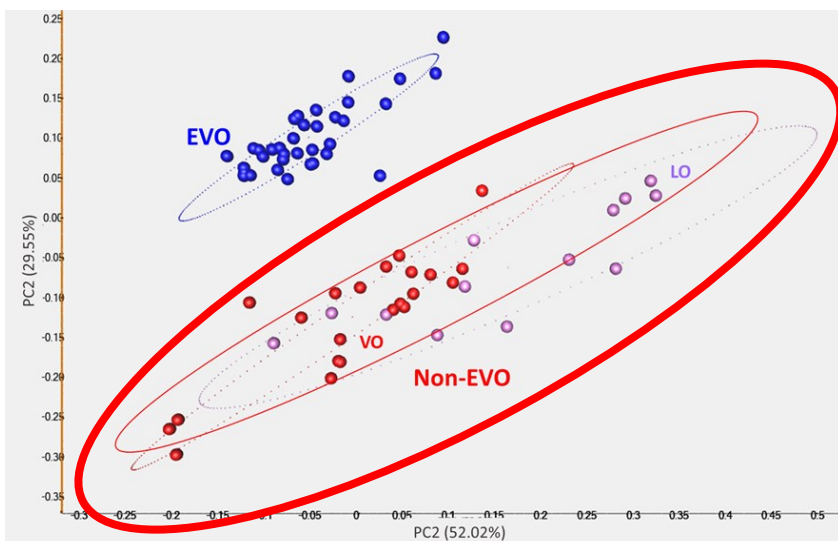
Extra Virgin
Virgin
Lampante



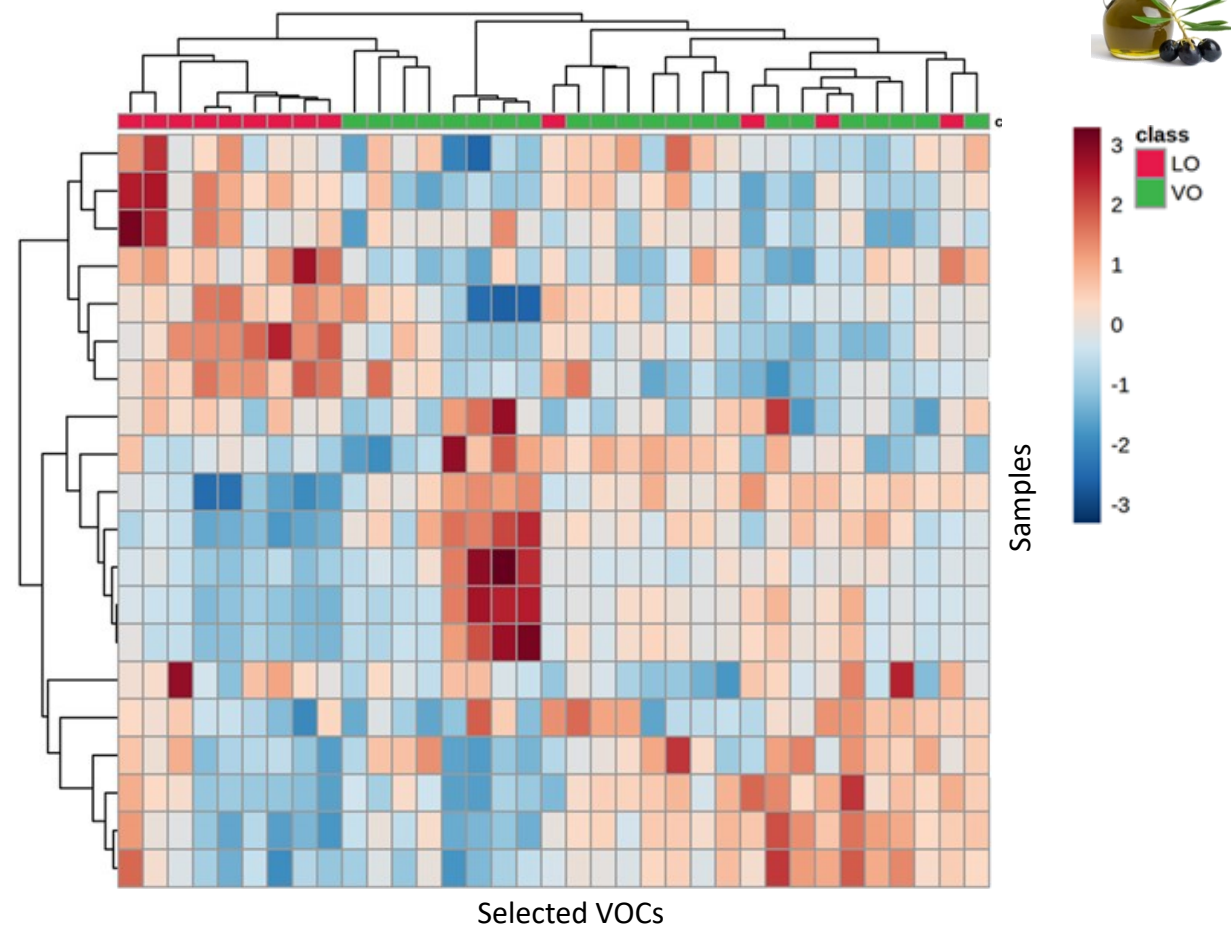
Cumulating extractions from same vial

69 Samples by 3×10min

34 EVO, 22 VO, and 13 LO



VO vs. LO
only



Different mode of HS extraction

- Pressure



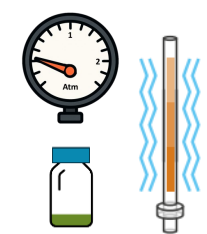
- Number of cumulated extraction

- Same vial
- Multiple vials

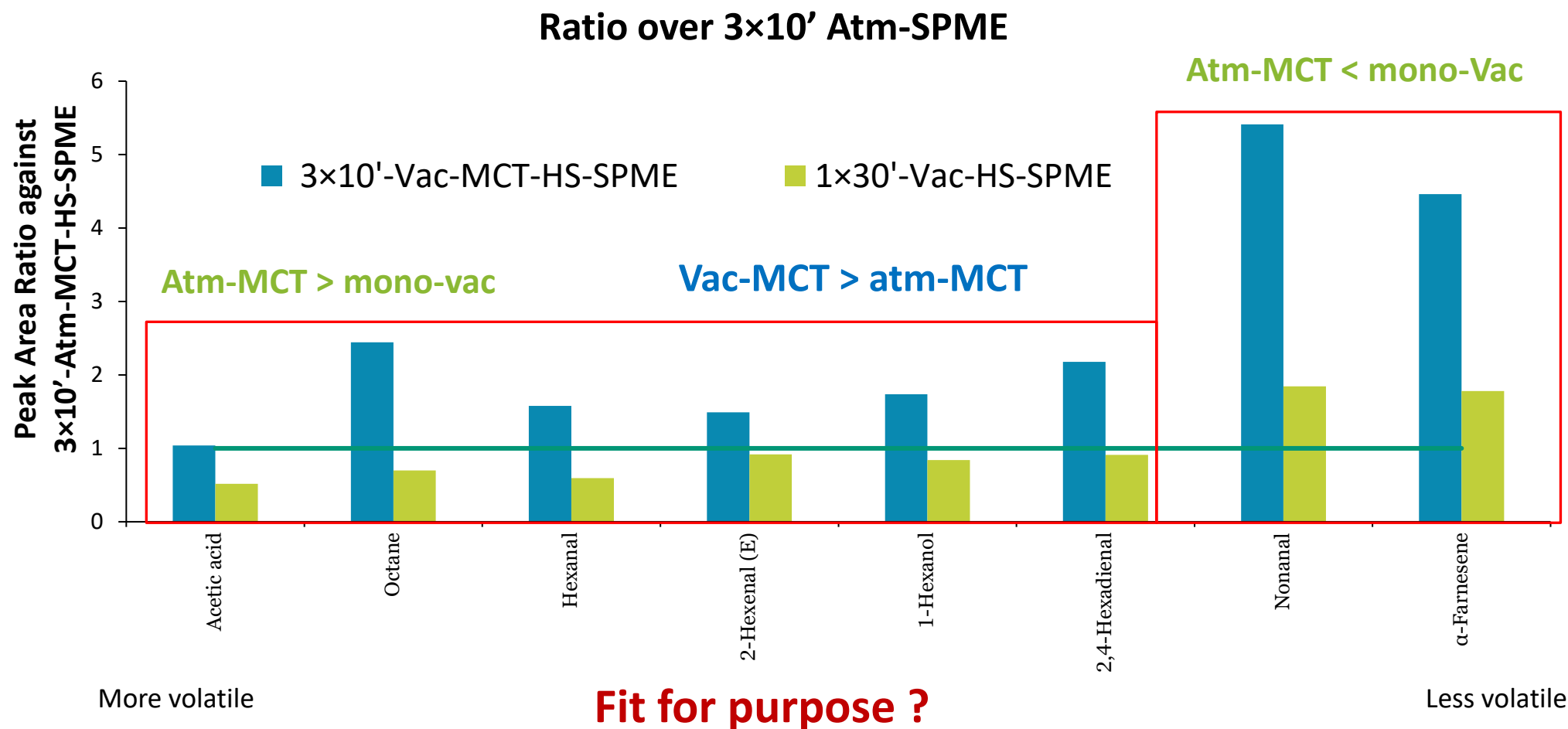


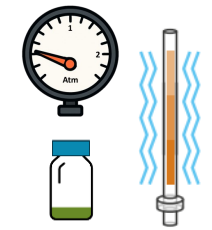
What if...?

Vac-multi cumulative
trapping-HS-SPME ?

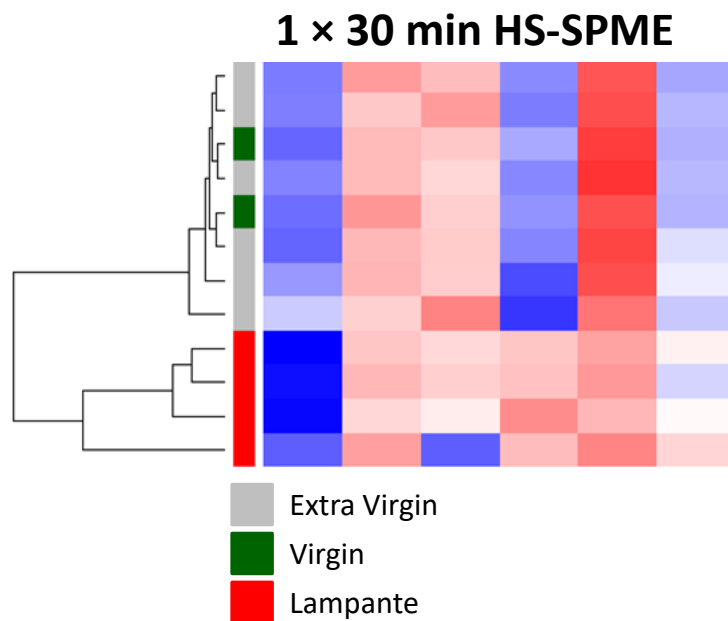


Cumulating both extractions and vacuum

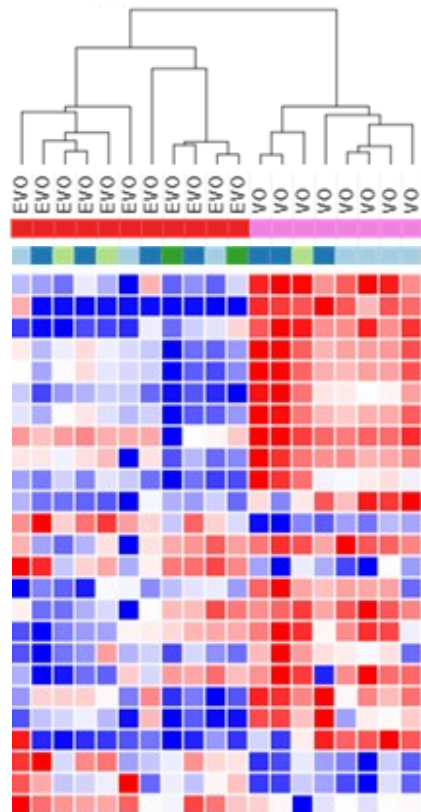




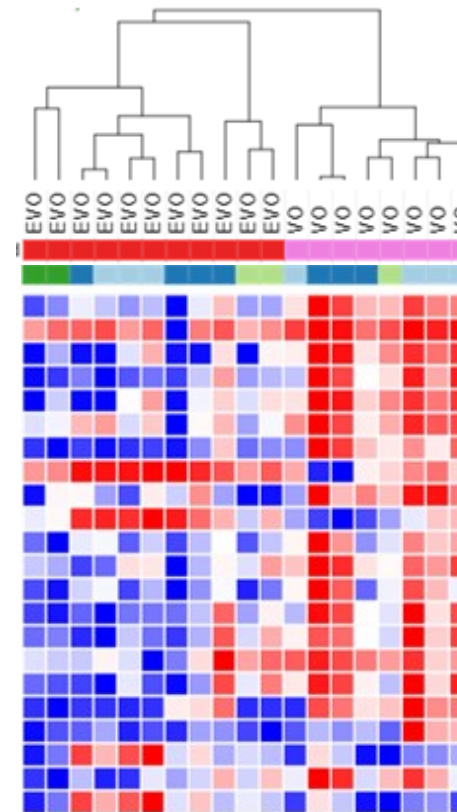
Cumulating both extractions and vacuum



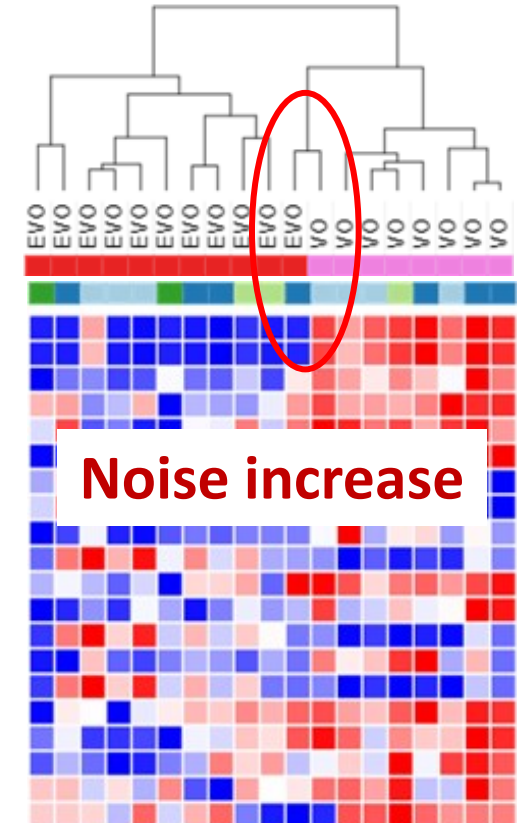
3 × 10 min HS-SPME



1×30min VAC-HS-SPME



3×10min-VAC-HS-SPME



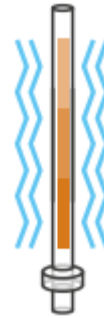
Different mode of HS extraction

- Pressure

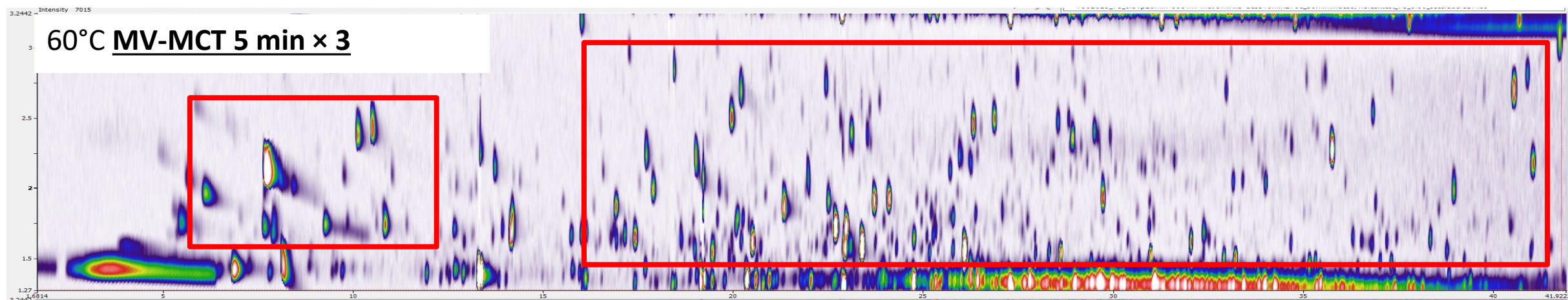
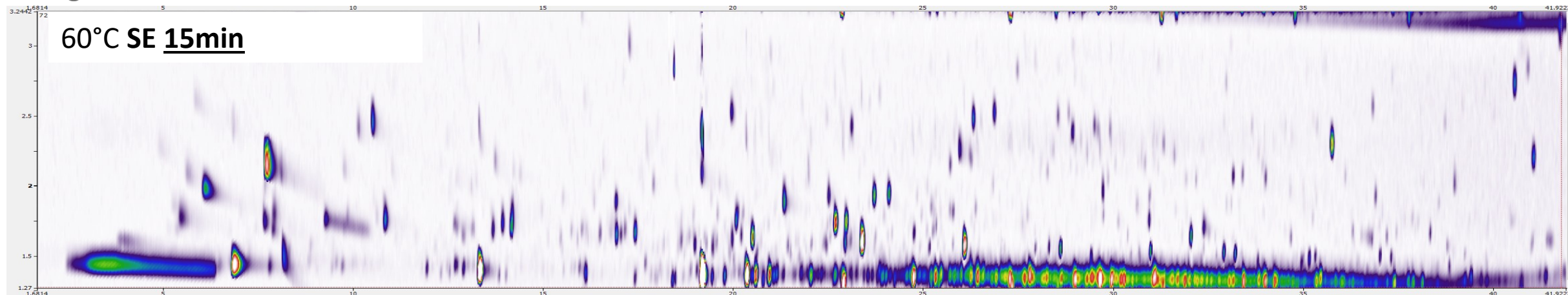
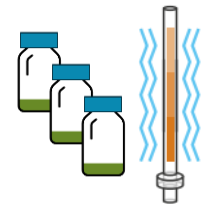


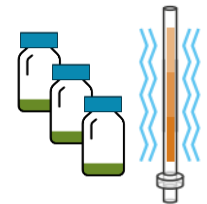
- Number of cumulated extraction

- Same vial
- Multiple vials



Cumulating extraction from different vials

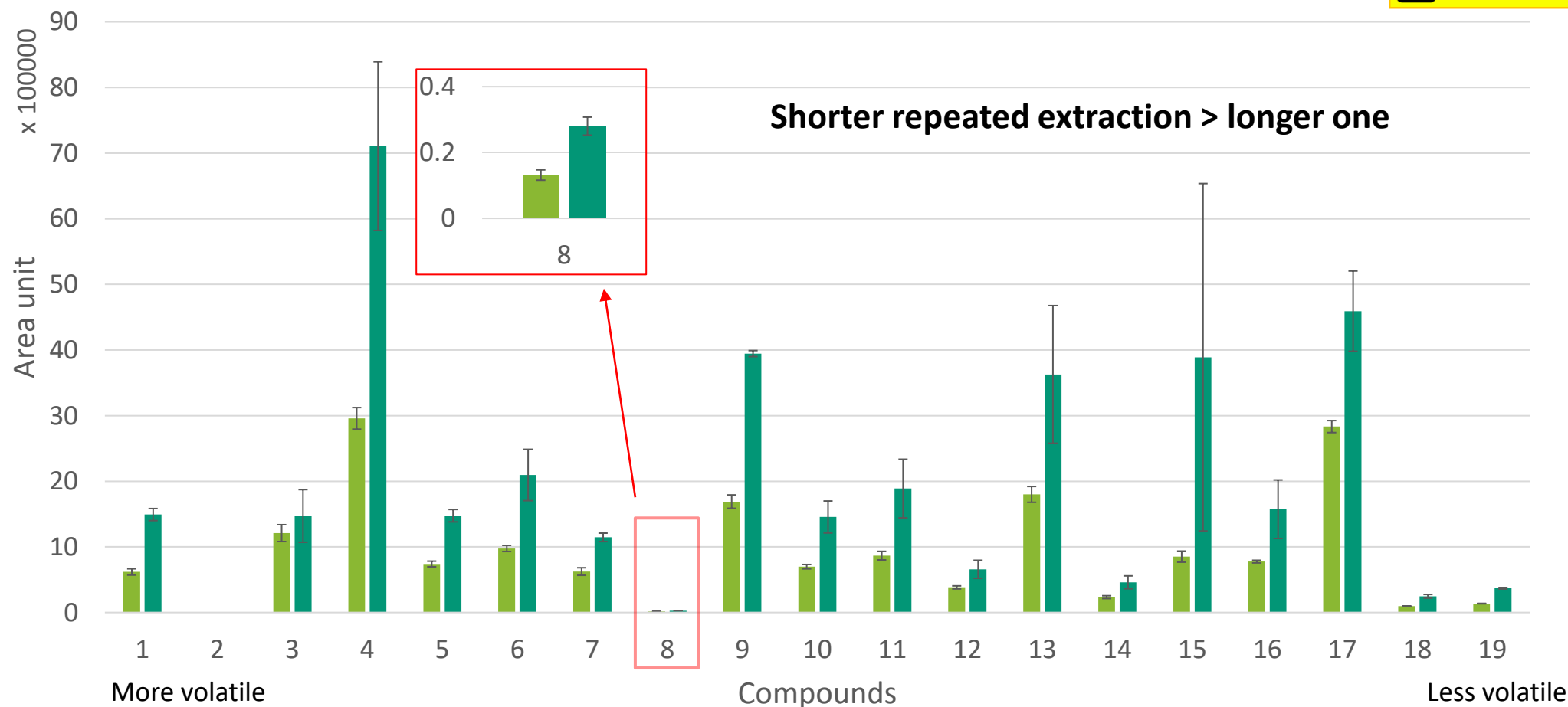




Cumulating extraction from different vials

1 × 15 min vs 3 × 5 min

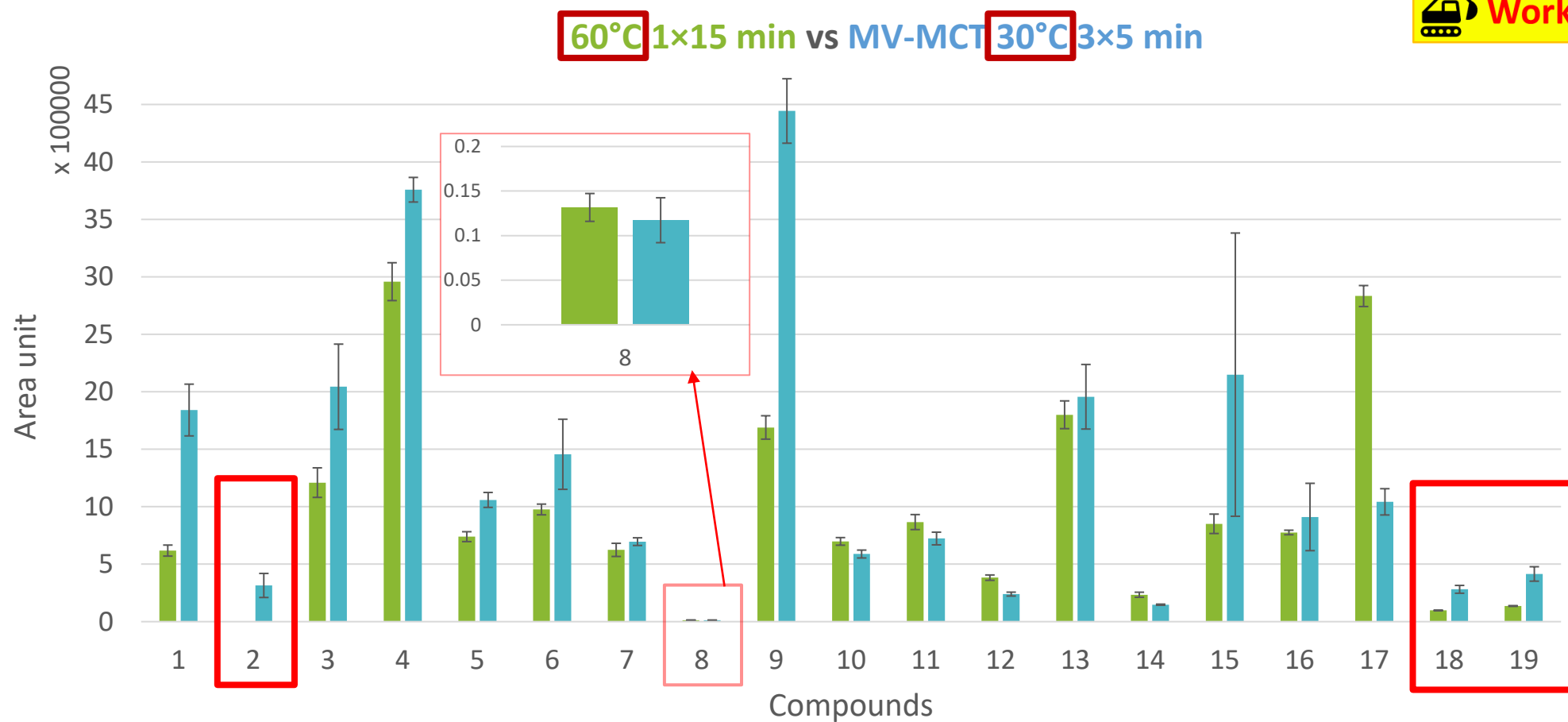
 **Work in progress**



Solid Samples at 60 °C

Cumulating extraction from different vials

 **Work in progress**



More volatile

Less volatile

Solid Samples

Key home message

- Playing with sampling tools and modes:
 - Selectivity
 - Sensitivity
 - Flexibility
 - Level of information

**Even more when
coupled with GC×GC!**

Thank you for your attention !



Analytical Chemistry GxABT :

Prof. Giorgia Purcaro

Sophie Vancraenenbroeck

Paula Albendea

Damien Eggermont

Aleksandra Gorska

Donatella Ferrara

Damien Pierret

Carlo Bellinghieri

Nicolas Ruin