BAM
Bundesanstalt für Materialforschung und -prüfung

Sicherheit in Technik und Chemie

Certech conference — 7 October 2021

DEVELOPMENT OF AN EFFICIENT PROCEDURE FOR THE ANALYSIS OF THE EMISSIONS OF VERY VOLATILE ORGANIC COMPOUNDS (VVOCS) IN EMISSION MEASUREMENTS FROM CONSTRUCTION PRODUCTS AND IN THE INDOOR AIR

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VVOC definition

Compounds that are more volatile than the VOCs, several definitions:

- **Boiling point** ranging from <0 °C to 50-100 °C *(WHO)*

- Elute before n-hexane on a 5% phenyl / 95% methyl-polysiloxane **GC column** *(ISO 16000-6 / EN 16516)*

- VOCs: **Vapor pressure** >10 Pa *(Committee on the Effect of Climate Change on Indoor Air Quality and Public Health)*
  Possible VVOC definition vapour pressures of > 100 Pa or even > 1000 Pa (Not official - *Salthammer, Indoor Air (2016)*)

➢ **Boundary region between VVOCs and VOCs**

Examples of VVOCs

Bp: Boiling point

Pvap: Vapor pressure

RI: Retention index

	Compound	Bp (°C)	Pvap at 25°C (kPa)	RI
C_1	**Dichloromethane**	40.0	58.0	531
	Methanol	64.6	16.9	354
C_2	**Acetaldehyde**	20.1	120	381
	Methyl formate	31.7	78.1	401
	Ethanol	78.3	7.91	459
C_3	**2-Chloropropane**	35.0	68.7	477
	Propanal	48.0	42.3	511
	Acrolein	52.6	36.5	480
	Acetone	56.1	30.8	500
	Methyl acetate	56.8	28.8	515
	Isopropanol	82.3	6.05	516
	1-Propanol	97.2	2.8	568
C_4	**1,3-Butadiene**	-4.5	274	394
	Vinyl acetate	71.6	12	562
	n-Butanal	74.8	14.8	595
	2-Butanone	79.5	12.1	592
	tert-Butanol	82.4	5.43	507
C_5	**n-Pentane**	36.1	68.5	500
C_6	**3-methylpentane**	63.2	25.3	577
	n-Hexane	69.0	20.4	600

Examples of VVOC sources

Indoor VVOC sources are numerous:

- Infiltration from **outdoors** via windows or ventilation systems
- **Activities**: cooking, cleaning or disinfection, tobacco smoke, scented products or printing
- Emissions from **materials**: wooden products, polyurethane foam sealant, mattresses or photocatalytic paints
- **Reaction products**: after exposure to ozone or degradation products
- Emanation from the **humans** themselves after exhalation

VVOC guideline values

Compound	EU-LCI	NIK	AIR	CMR Classification
	(µg/m³)			
Dichloromethane			200/2000	Carc. 2
Methanol		-		
Acetaldehyde	1200	1200	100/1000	Carc. 1B, Muta. 2
Methyl formate	-			
Ethanol		-		
2-Chloropropane		(800)	800/8000	
Propanal	650	750		
Acrolein		14		
Acetone	120000	1200		
Methyl acetate		-		
Isopropanol		-		
1-Propanol		-		
1,3-Butadiene				Carc. 1A, Muta. 1B
Vinyl acetate		-		Carc. 2
n-Butanal	650	650	100/2000	
2-Butanone	20000	20000		
tert-Butanol	620	620		
n-Pentane		-		
3-methylpentane		-		
n-Hexane	4300	4300		Repr. 2⁺

-: on the working or waiting list

EU-LCI/NIK: Lowest concentration of interest

AIR: German committee on indoor air guide values

VVOC measurement methods

- ISO 16000-3 for carbonyls

- ISO 16000-6 (2021):
- Use of **gas standards** recommended
- **Different sorbent materials** (graphitized carbon blacks, carbon molecular sieves, multi-sorbents) discussed
- More care with respect to **column selection** required
(ISO 16000-6:2011: longer column and/or thicker film)
- Advises to apply a **purge** before tube desorption

➢ **Only suggestions** – no experimental evidence of operability

Current BAM project

Research plan of the Federal Environment Agency (UBA) – grant n°3719 62 209 0

"Development and validation of a high-performance method for the determination of very volatile organic compounds (VVOCs) in emission measurements from construction products and in the indoor air"

Started January 2020

- **Aims at exploring possibilities to sample and analyze VVOCs via thermal desorption coupled to GC/MS**

Need for an adequate analysis method

1) **Gas standards**

2) Suitable column

3) Suitable adsorbents

4) Water management strategy

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1) Gas standards – A necessity

Stronger adsorbents used
→ **Solvent can no longer be flushed** prior to analysis

- **Competition** with the target analytes on the sorbent
- Solvent must be **masked** during detection (can no longer be an analyte itself)
- Difficult **handling** during solution preparation (very volatile compounds)

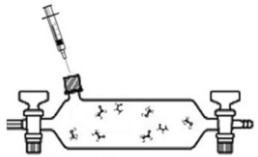
- **Need for gas standards**

1) Gas standards – Current project

Substance selection criteria :

- EU-LCI / NIK / AIR values or working lists, toxicity
- Presence in emission and/or indoor measurements (literature)
- 60 substances (47 VVOCs + 13 VOCs in the boundary region)

Commercial gas mixes
for gaseous substances (21)



Liquid substances (44) dissolved in each other in groups and doped in gas collecting tubes

Cross-checked for 5 substances
+ reactivity tested

Need for an adequate analysis method

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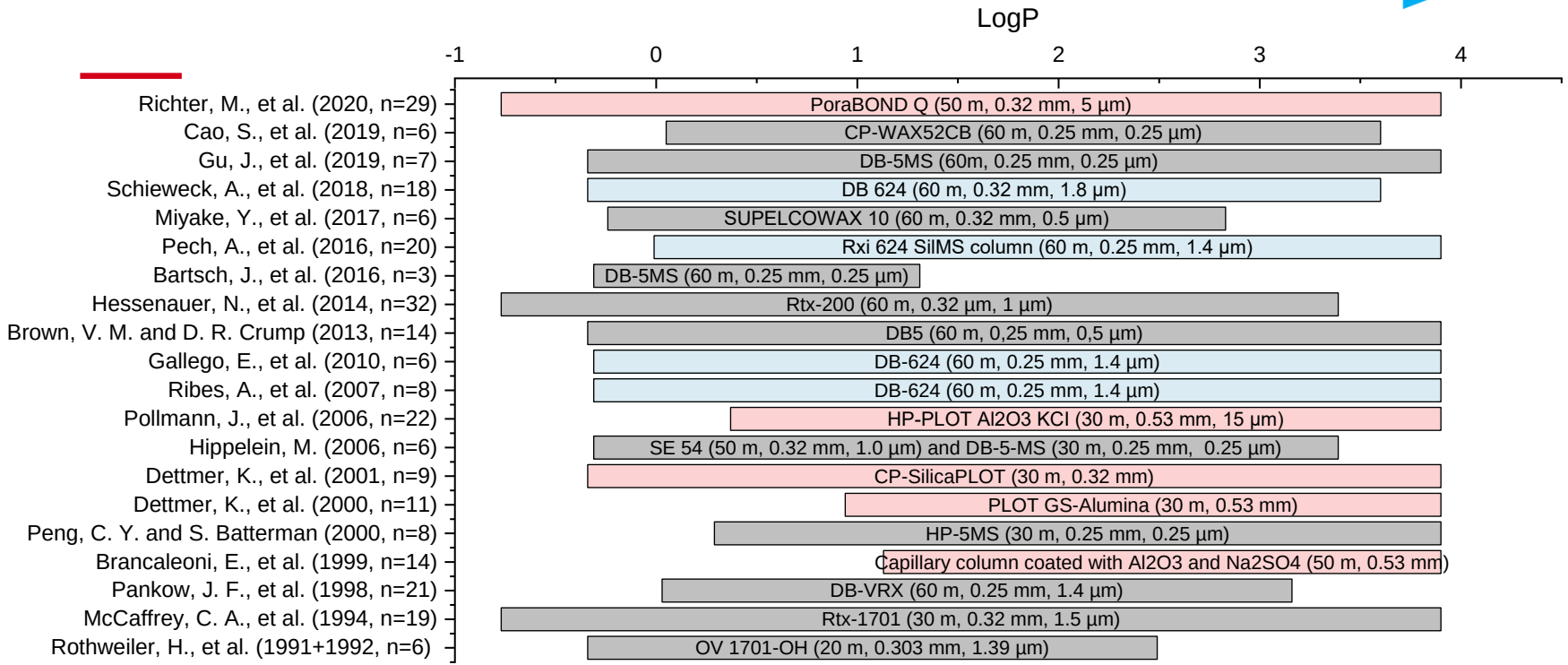
2) Suitable column - Literature

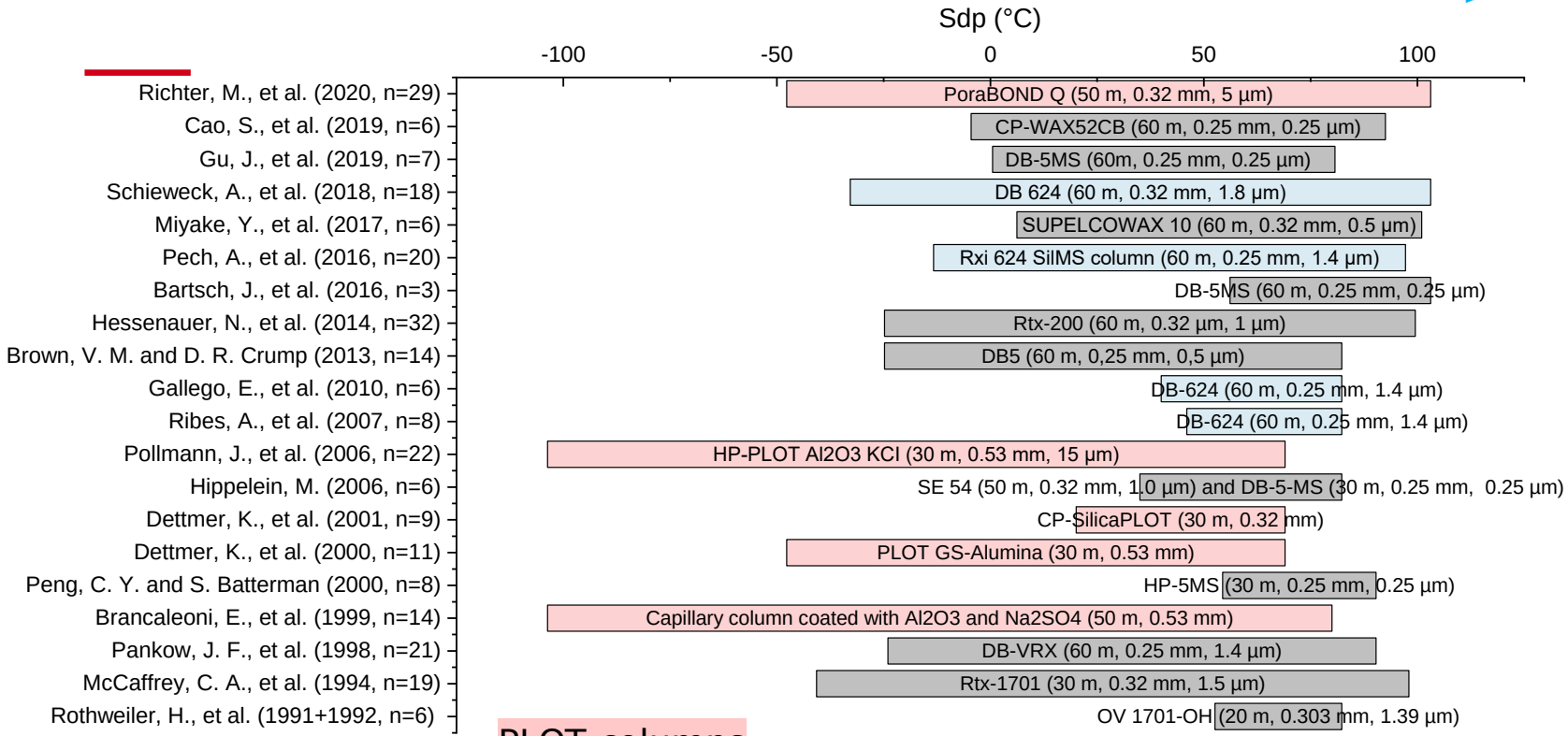


PLOT-columns

624-columns

Even, M., E. Juritsch, and M. Richter. Trends in Analytical Chemistry, 140 (2021).
https://doi.org/10.1016/j.trac.2021.116265

2) Suitable column - Literature



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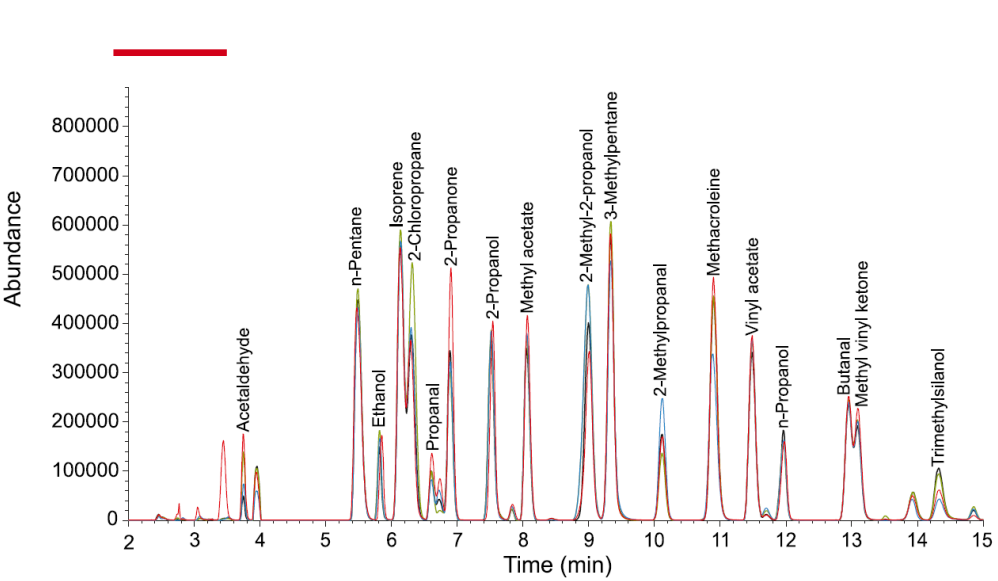
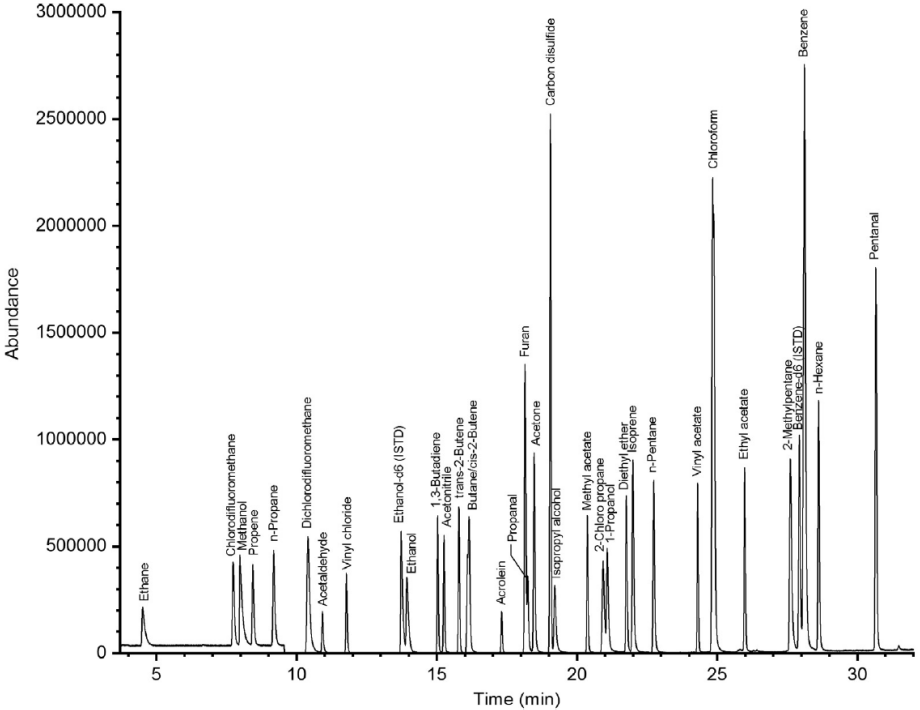




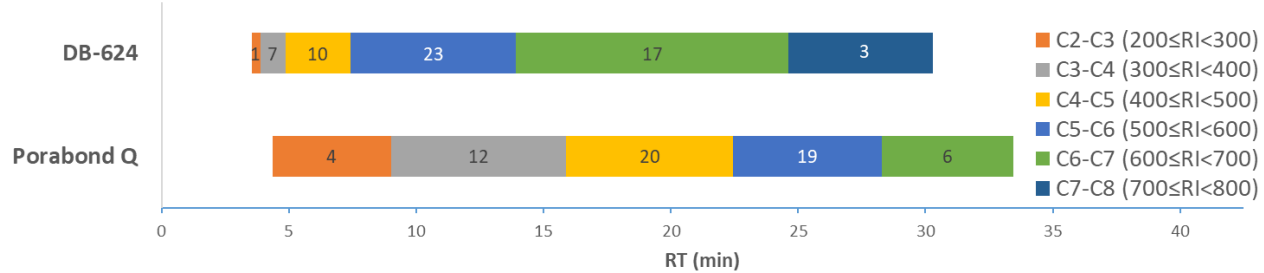
DB-624 (60 m × 0.32 mm × 1.8 µm)

Schieweck et al., Anal. Bioanal. Chem. (2018)

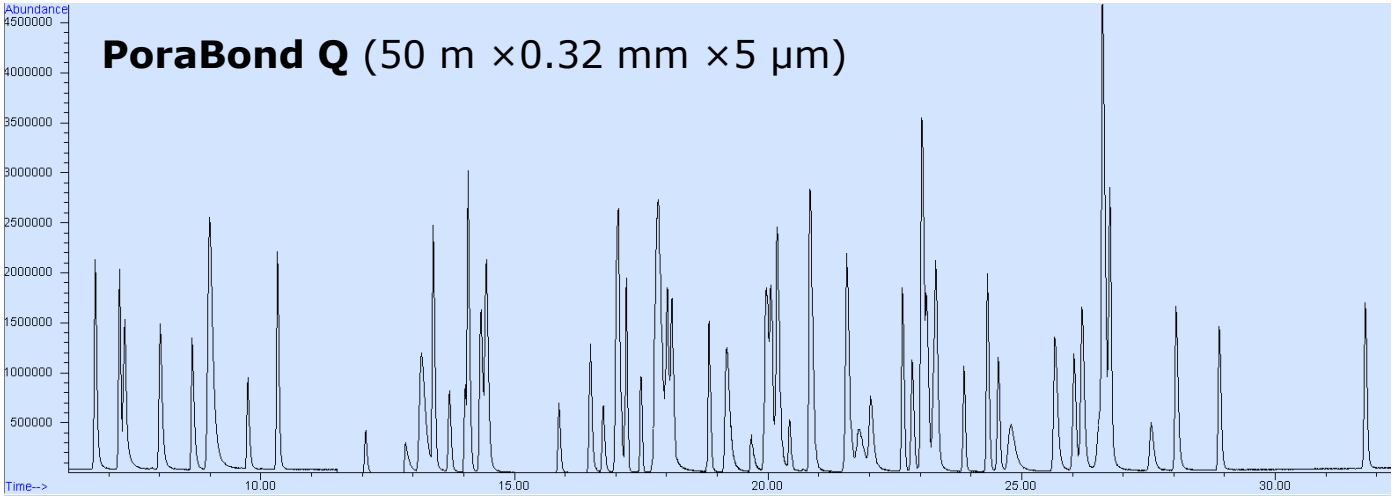
PoraBond Q (50 m ×0.32 mm ×5 µm)

Richter et al., J. Chromatogr. A (2020)

2) Suitable column – Current project



61 analytes



PoraBond Q (50 m ×0.32 mm ×5 µm)

Need for an adequate analysis method

1) Gas standards

2) Suitable column

3) Suitable adsorbents

4) Water management strategy

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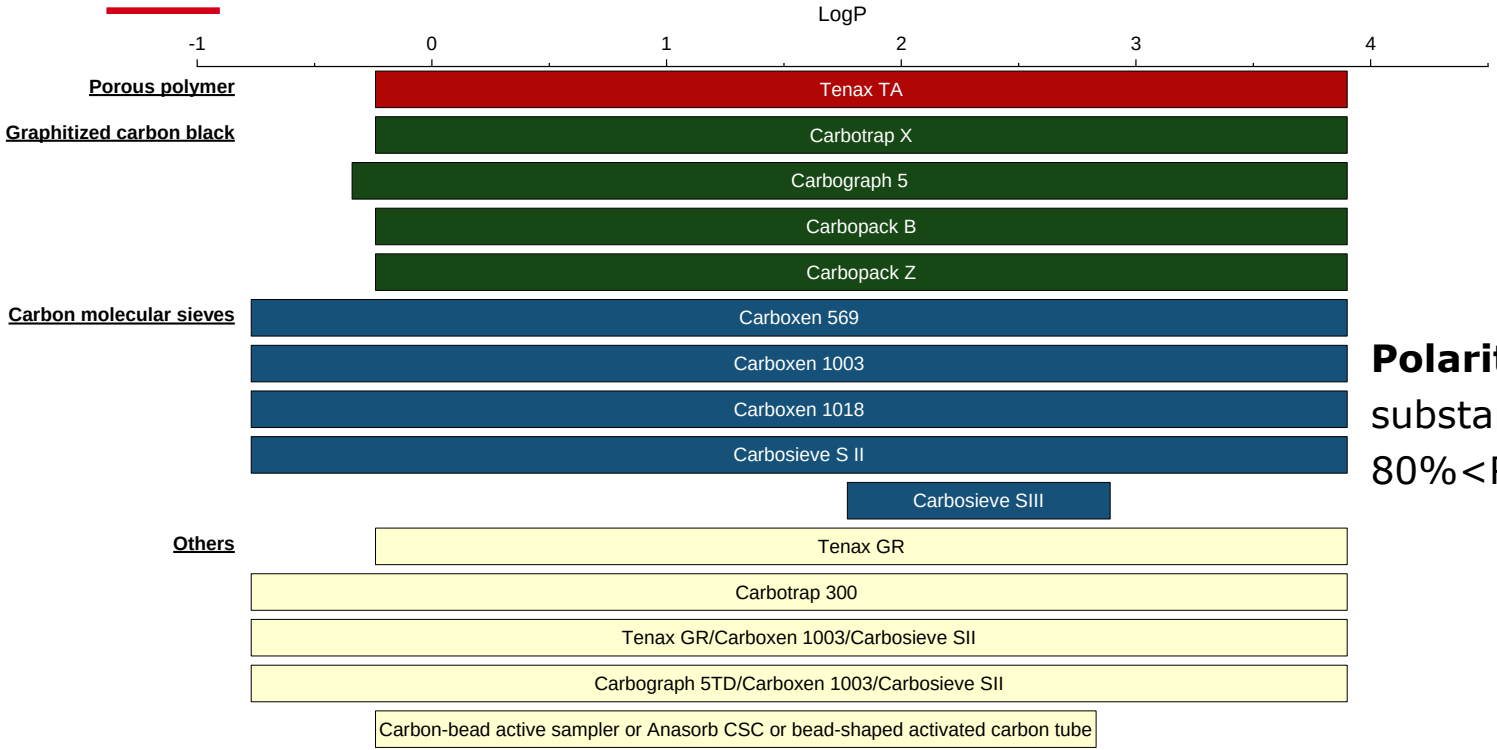
3) Suitable adsorbent - Literature



Polarity range of the substances with 80%<Recovery rate <120%

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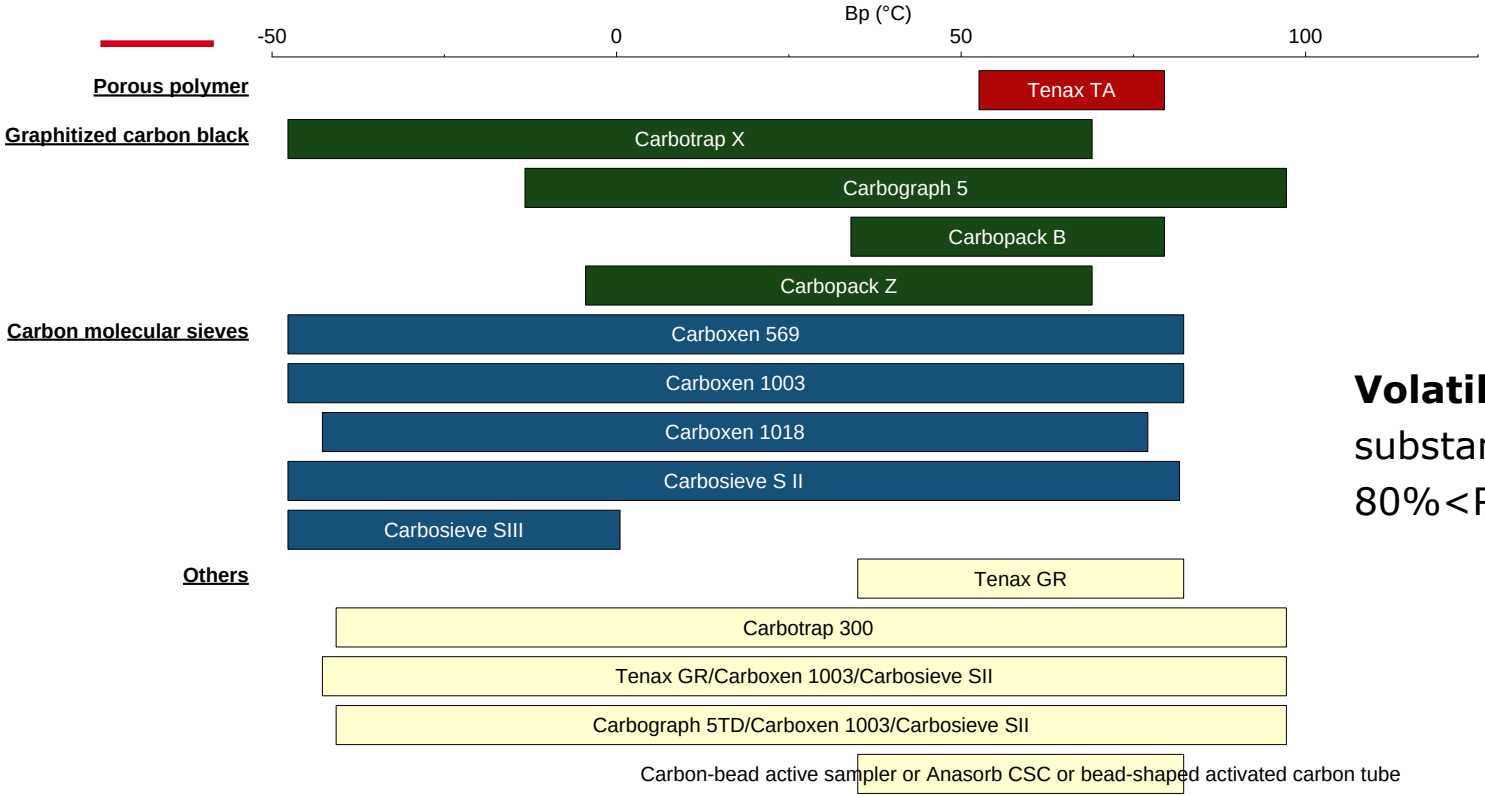
3) Suitable adsorbent - Literature



Volatility range of the substances with 80%<Recovery rate <120%

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3) Suitable adsorbent - Literature

- *Schieweck et al., Anal. Bioanal. Chem. (2018) : Comparison of different adsorbents*

➢ **Carbograph 5TD** suitable for C3-C6

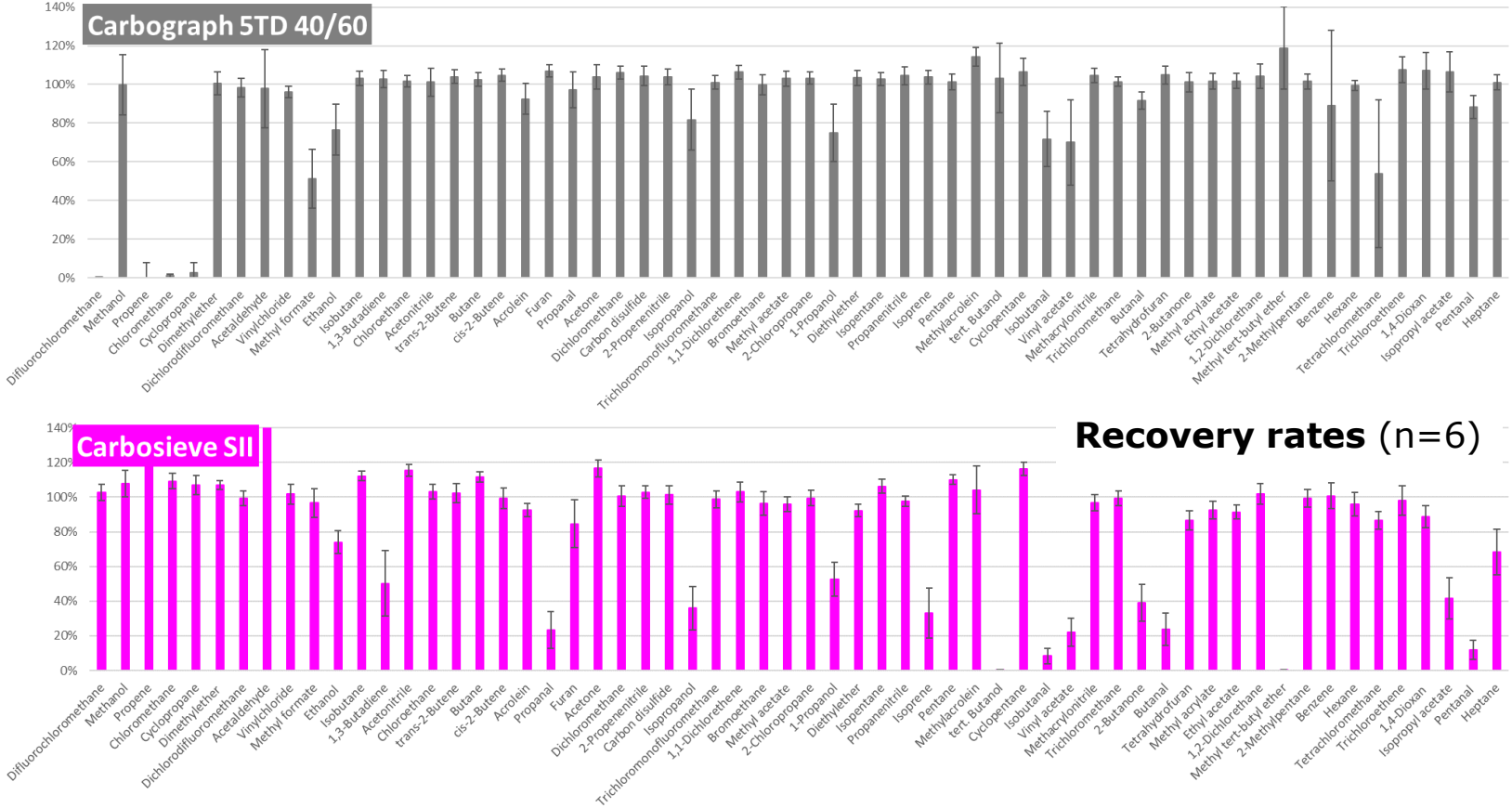
➢ Need for another adsorbent for C1-C2

- *Richter et al., J. Chromatogr. A (2020)*: *Consideration of the recovery and the relative humidity*

➢ **Combinations**

Carbograph 5TD + Carboxen 1003 + Carbosieve SII
and **Tenax® GR + Carboxen 1003 + Carbosieve SII**
potentially suitable for a gas mixture with 32 substances

3) Suitable adsorbent – Current project



Need for an adequate analysis method

1) Gas standards

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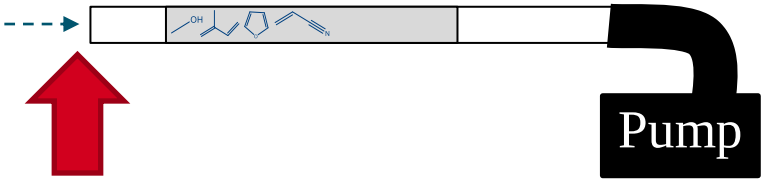
4) Water management strategy

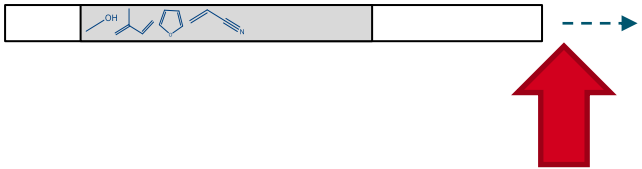
Carbon molecular sieves are hydrophilic

Water removal:



Aim: No/little water on the tube

Prior to sampling



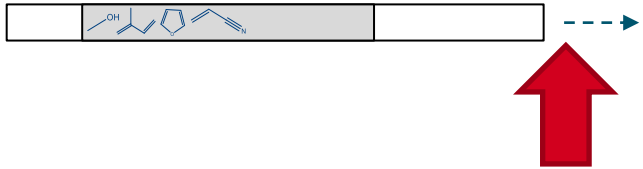
Aim: Remove water from the tube

After sampling

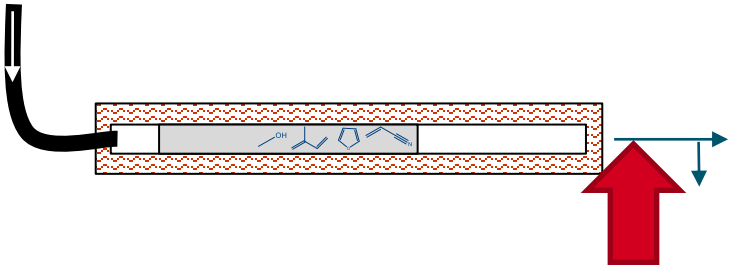
4) Water management strategy

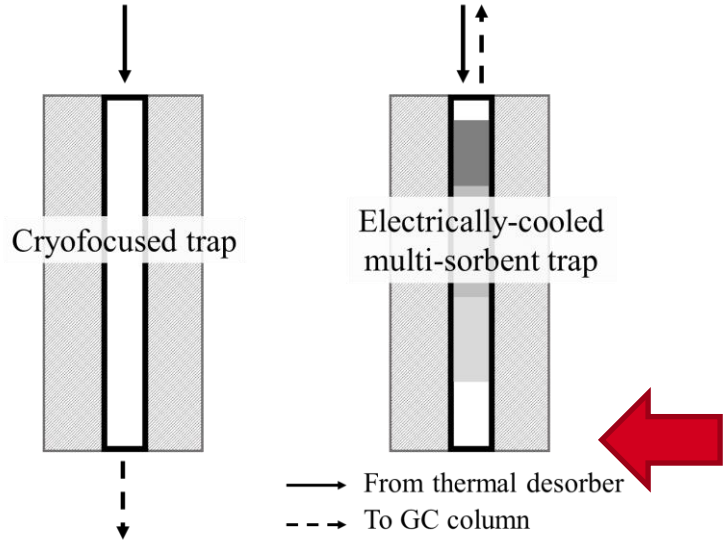
After sampling

- Purge (Sorbent + Trap)



- Split





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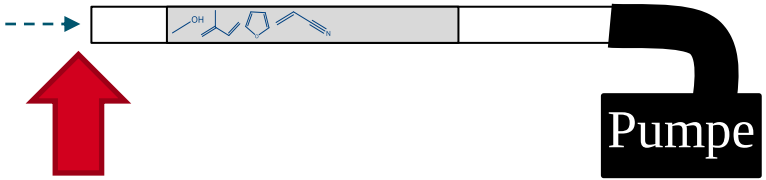
➢ **Drawbacks: Losses, competition between analyte and water on the tube**

4) Water management strategy

Prior to sampling



- **Drying agents**:

Silica gel, Nafion (+ K_2CO_3), Molsieb 3A, Na_2SO_4 , $CaSO_4$, CaH_2, $CaCl_2$, $MgSO_4$, $Mg(ClO_4)_2$, NaOH + K_2CO_3 , P_2O_5 , Al_2O_3

→ Amount? Holder?

- **Water trap** (Peltier cooling)

➢ **Possible lost of analytes**

Conclusion

Analysis of VVOCs by TD-GC/MS in analogy to VOC measurements following ISO 16000-6 is feasible but requires many adaptations:

- **Gas standards** are needed
- **Porabond Q** GC column is suitable for VVOC analysis
- **Carbograph 5TD** should be **combined with stronger sorbent** to cover the whole VVOC range
- A **reliable method for water removal** is needed

Thank you for your attention!

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