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Reflexions on the existing guideline (and EN) about the sampling and analysis of tar matter from product gas, pyrolysis gas and synthesis gas

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Milan, 21.06.2012

Application of CEN/TS 15439

Sampling-conditions at measurement point:

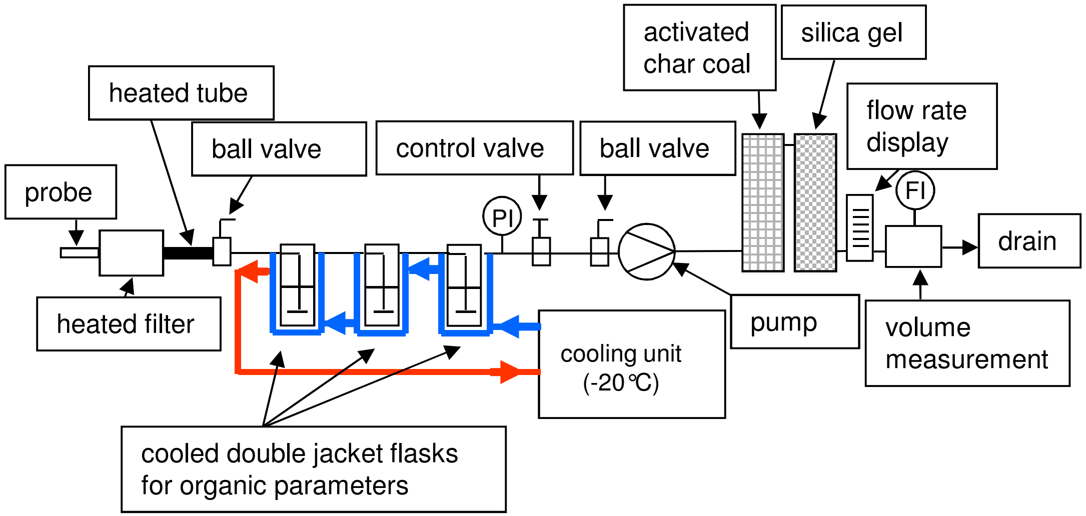
pressure	[kPa]	60 - 6 000
temperature	[°C]	0 - 900
tar loading	[mg/m³ₙ]	1 – 300 000
dust loading	[mg/m³ₙ]	20 – 30 000

Received values:

gravimetric tar	[mg/m³ₙ]
concentration of individual org. compounds	[mg/m³ₙ]
sum of GC-detactable tar calculates as naphthalene	[mg/m³ₙ]
dust concentration	[mg/m³ₙ]

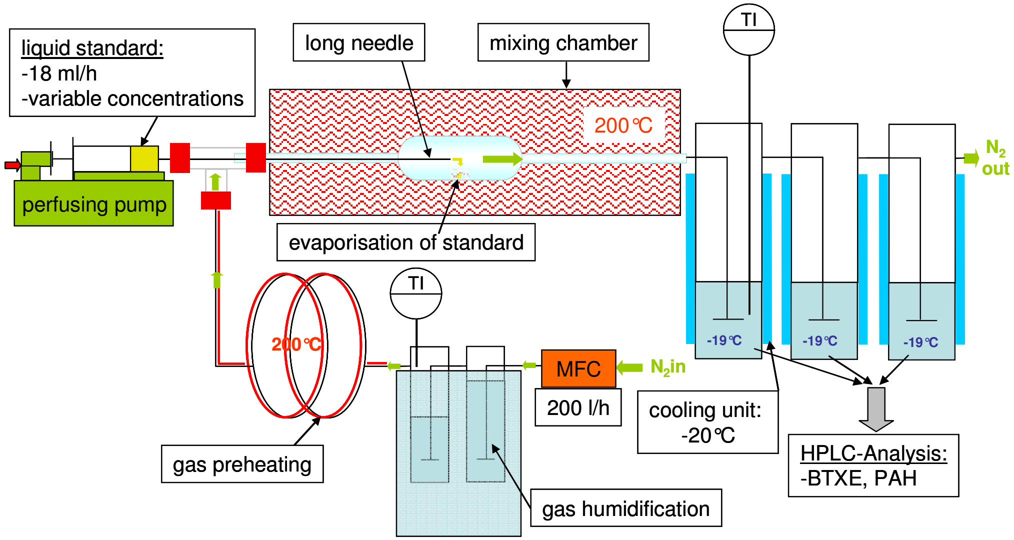
Instructions for: reagents, equipment, preparation, sampling, storage, analysis, calculations, dimensions

Equipment at Bioenergy2020+

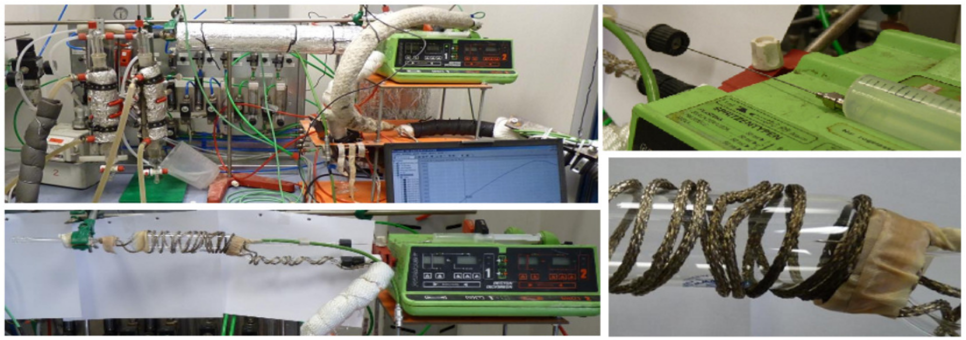


- probe: stainless steel, PTFE, glass
- heated filters: planar or depth
- absorption columns: cooled (-20℃)
- pump: membrane pump
- gas drying/cleaning: silica, activated carbon
- volume detection: diaphragm gas-meter

Quality measures – multi component gas-generating unit



- gas flow: 50-500 l/h
- gas humidification: 20-90°C (saturation)
- gas preheating: 120°C
- dosage of liquid standard: 0.1 to 50 ml/h
- vaporisation temperature: 200°C
- absorption units: cooled down to max. -19°C; 100 ml 2-propanol each



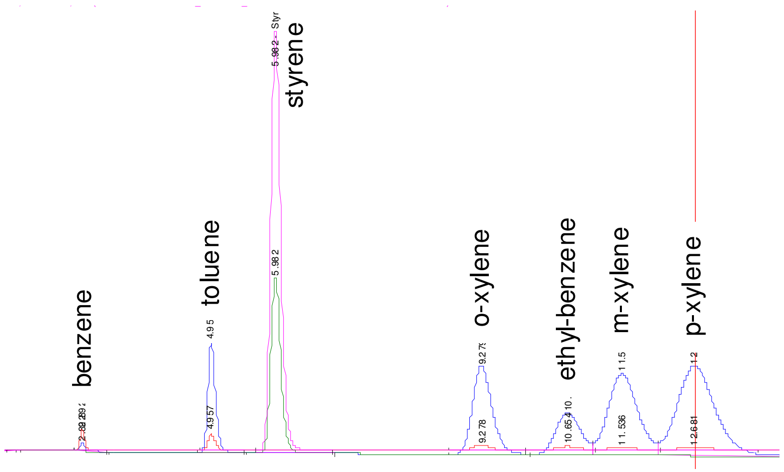
- tested substances: BTX(o,m,p)E-S, PAH (naphthalene to crysene), aldehydes, terpenes
- tested absorbance solutions: 2-propanol, acetonitrile (+addition)
- result:

$$y[\%] = \frac{m_{abs}}{m_{input}} * 100$$

HPLC-analysis

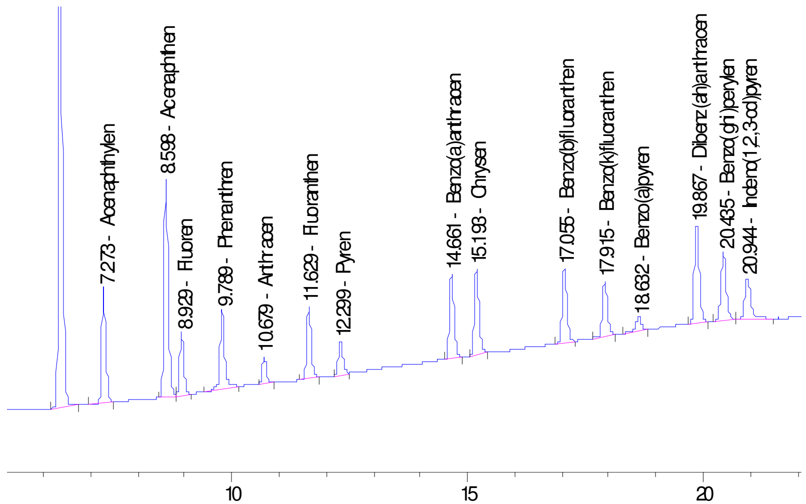
BTXE-S:

- Column: Zorbax Eclipse PAH, 4.6x150 mm; 3.5 µm; plus precolumn
- Injection: 10µl, Flow: 2ml/min
- Detection: MWD: 220nm; 254nm (benzene, styrene)
- Solvent: 0-1min 45% acetonitrile, 55% water; 1-15min gradient to 25% acetonitrile, 75% water

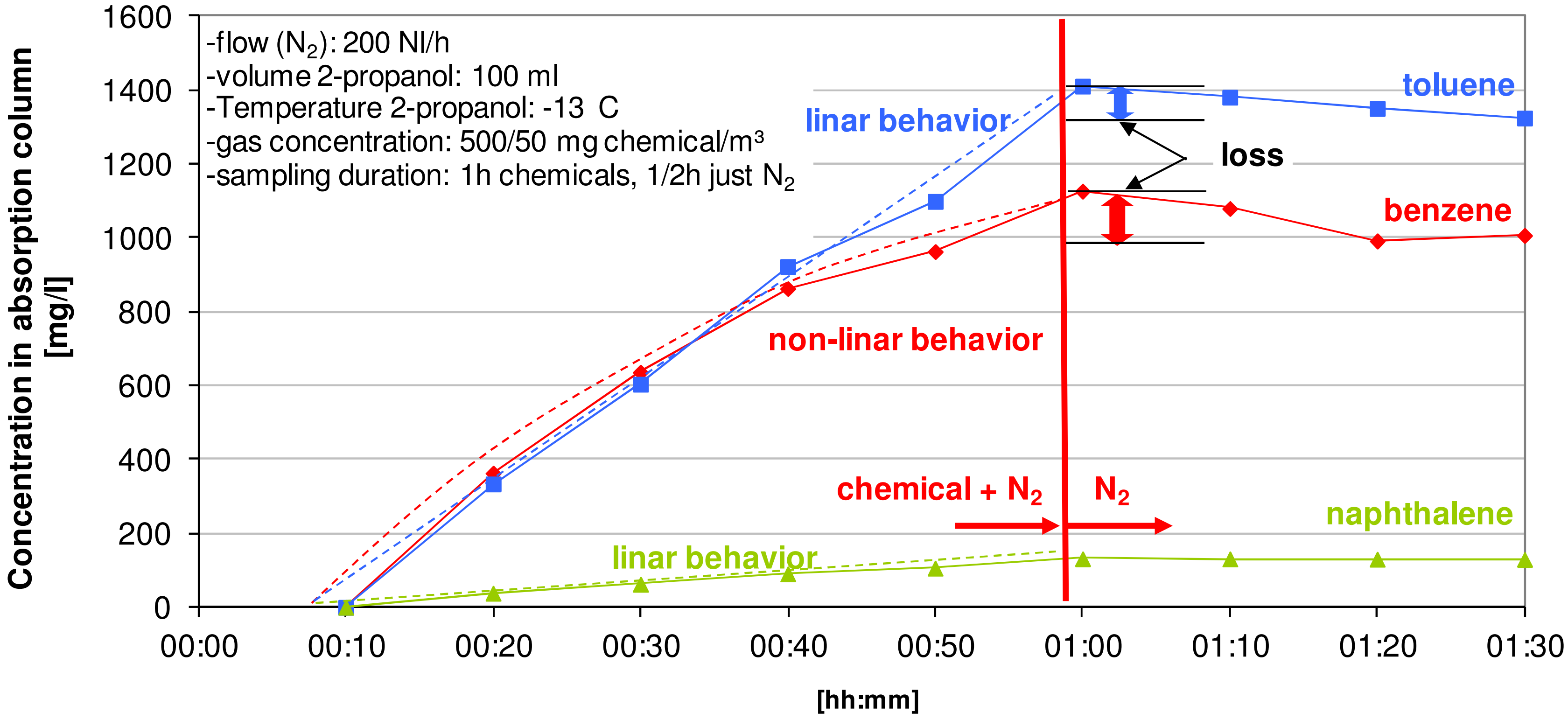


PAH:

- Column: Zorbax Eclipse PAH, 4.6x150 mm; 3.5 µm; plus precolumn
- Injection: 10µl, Flow: 2ml/min
- Detection: MWD: 220nm
- Solvent: 0-0.66min 40% acetonitrile, 60% water; 0.66-20min gradient to 100% acetonitrile, 20-25min 100% acetonitrile; 25-27min gradient to 40% acetonitrile 60% water; 27-30min 40% acetonitrile, 60% water



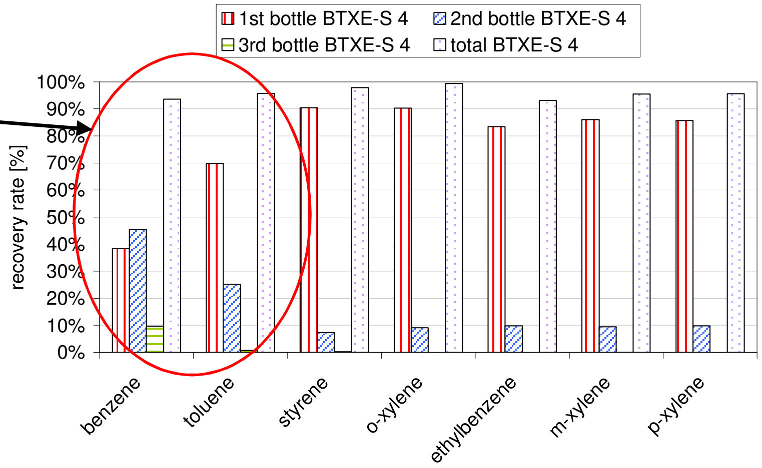
Dynamic behaviour of benzene, toluene and naphthalene in 2-propanol

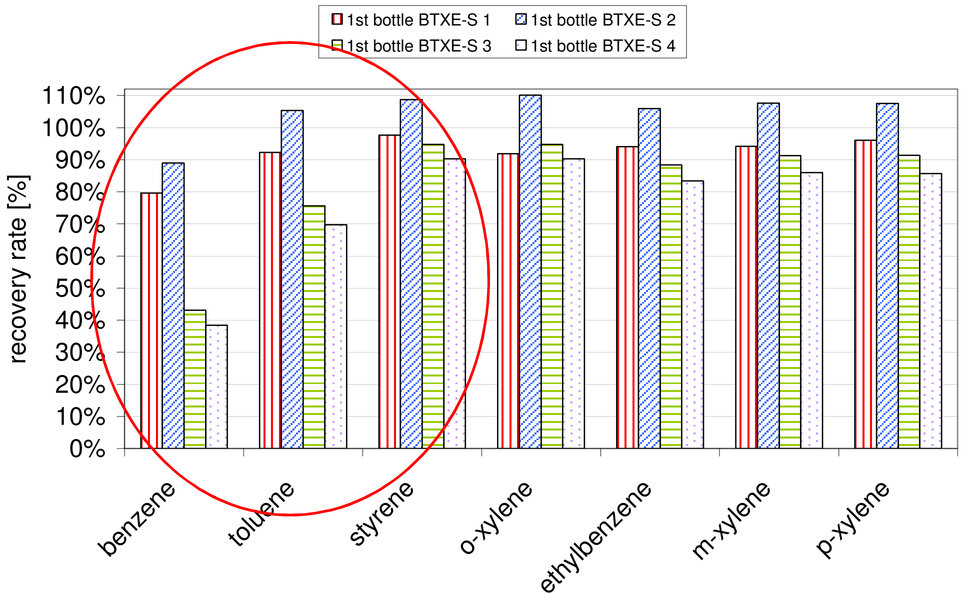


Results – BTXE-S-tests (4 runs)

Settings:

	BTXE-S 1	BTXE-S 2	BTXE-S 3	BTXE-S 4
T 1st bottle [°C]	-15	-15	+14	+7
T 2nd bottle [°C]	-15	-15	-15	-15
T 3rd bottle [°C]	-15	-15	-15	-15
carrier gas flow [l/h]	200	200	200	200
water loading [$kg/kg_{gas,dry}$]	-	-	-	0,05
gas-concentration [mg/m³]	85-110	75-97	80-103	85-108
concentration 1st bottle [mg/l]	106-148	103-146	58-151	47-128



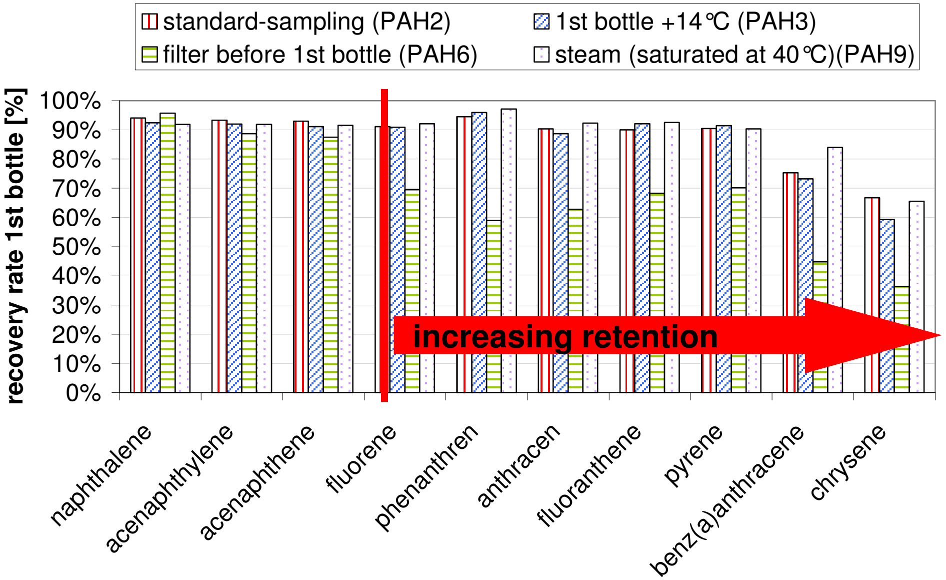


- **Findings:**
  - temperature-influence (cooling):
    - Strongest influence on benzene and toluene
    - at -15°C: 80% in 1st bottle
    - at +10°C: 40% in 1st bottle
  - Solvent suitability:
    - 2-propanol suitable for all BTXE-S
    - at -15°C: 2 columns sifficient

Results – PAH-tests (9 runs)

Settings:

	PAH 1	PAH 2	PAH 3	PAH 4	PAH 5	PAH 6	PAH 8	PAH 9
T 1st bottle [°C]	-15	-12	+14	-12	-12	-12	+7	+7
T 2nd bottle [°C]	-15	-12	-12	-12	-12	-12	-12	-12
T 3rd bottle [°C]	-	-12	-12	-12	-12	-12	-12	-12
carrier gas flow [l/h]	200	200	200	200	200	200	200	200
water loading [$kg/kg_{gas,dry}$]	-	-	-	-	-	-	0,05	0,05
filtering (planar filter)	-	-	-	x	x	x	-	-
gas-concentration [mg/m³]	3.6 - 4.6 (naphthalene 20)							
concentration 1st bottle [mg/l]	2 - 6 (naphthalene 20 - 30)							



- **Findings:**
  - temperature-influence (cooling):
    - no difference -15/+7°C
  - temperature-influence (heating):
    - for larger PAH (>fluorene) temperature 350 – 450°C
    - Danger of condensation at T<400°C
  - solvent suitability:
    - 2-propanol suitable for all PAH
    - generally over 90% in 1st column
    - 2 columns sufficient enough

Results – sample storage

Questions:

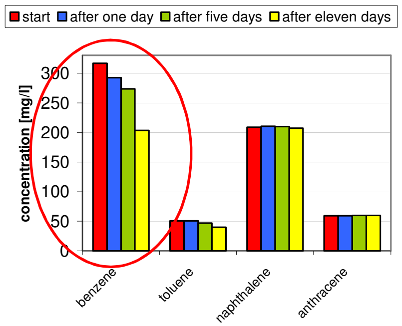
- How long can benzene/toluene/naphthalene/anthracene be stored before analysing?
- Has the water-content of the 2-propanol sample an influence on the storage-duration?
- Is it possible to stabilise the samples?

Settings:

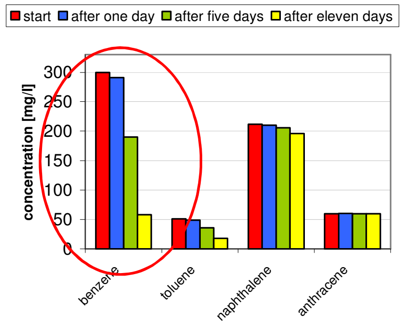
	benzene	toluene	naphthalene	anthracene
initial concentration [mg/l]	292	50	206	58
variation of water [$\%_{vol}$]	5,10,20,30			
variation of acetone [$\%_{vol}$]	5,10,20			

Results:

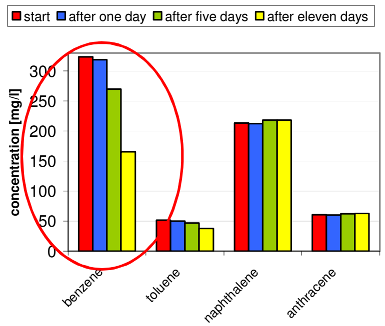
5% water in 2-propanol
(storage-temperature: 2°C)



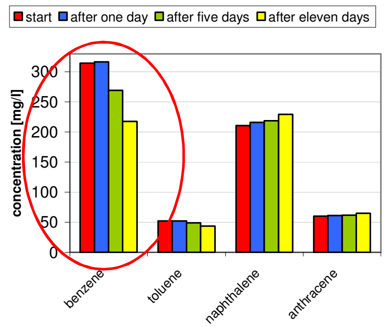
30% water in 2-propanol
(storage-temperature: 2°C)



5%acetone in 2-propanol
(storage-temperature: 2°C)



20%acetone in 2-propanol
(storage-temperature: 2°C)



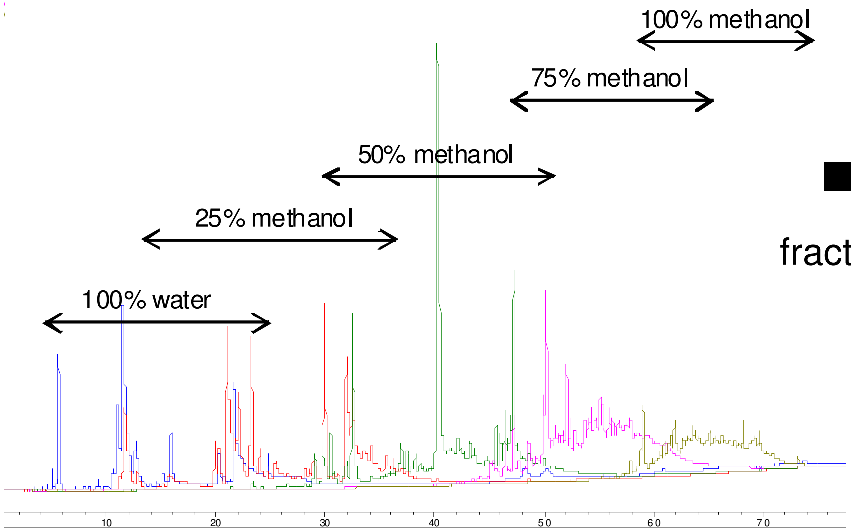
Summary

- <u>Sampling:</u>
  - BTXE-S:
    - 100 mg/m^3 BTXE-S in gas → sampling conditions:
      - 3-columns in a row with 100 ml 2-propanol each
      - Gas-flow: 200 l/h
      - Cooling temperature <-13°
      - Sampling duration: 1 h
  - PAH:
    - 5 mg/m^3 PAH (naphthalene to crysene) in gas → sampling conditions:
      - 2-columns in a row with 100 ml 2-propanol each
      - Gas-flow: 200 l/h
      - Cooling temperature 0℃ sufficient
      - Sampling duration: 1 h or longer
      - Heating of filter/tube: at least 350° (for largest PAH probably not sufficient)
- <u>Storage/analysis:</u>
  - BTXE-S: storage-temperature: 2-8℃ (or even cooler); analysis: next day
  - PAH: storage-temperature: 2-8℃ (sufficient); analysis: at least 11 days stable

Fractioning of pyrolysis-samples for identification of main components

5 fractions:

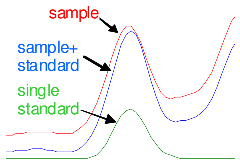
SPE:



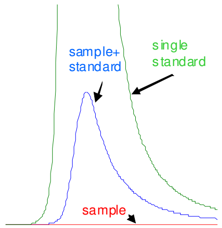
fractioning

identification

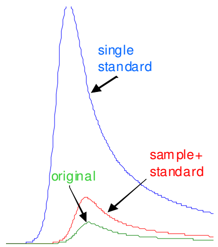
HPLC:



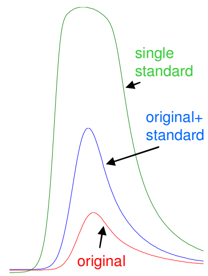
Levoglucosan



Eugenol



Furfural



Guaiacol

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Thank you for your attention!

Further questions? Please contact:

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Milan, 21.06.2012

Thermodynamic fundamentals of accumulation

- Physical fundamentals and data of selected tars
  - Mechanisms and data
  - Pure substances
  - Gas/Liquid-systems (VLE)
- Test of a single stage accumulator
  - Mass transfer and VLE
- Further information to be useful
  - Standardised characterisation of separators
  - VLE-data for solvents/PAH (PAH-S)
  - Capture and break through curves

Physical fundamentals

Phase change thermodynamic of **pure** substances:

Vapour← → Liquid: condensation and evaporation

‚activity gas= activity liquid‘

$$p_i = p_{total} \cdot y_i \cdot \varphi_i \big|_{gas} = p_i^* \cdot x_i \cdot \gamma_i \big|_{liquid}$$

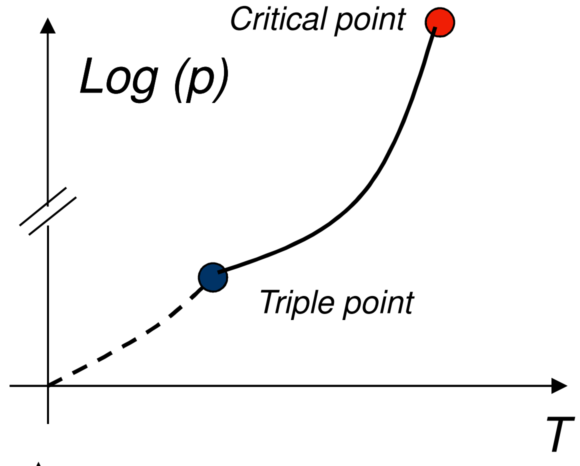
Vapour ← → Solid: re-sublimation and sublimation

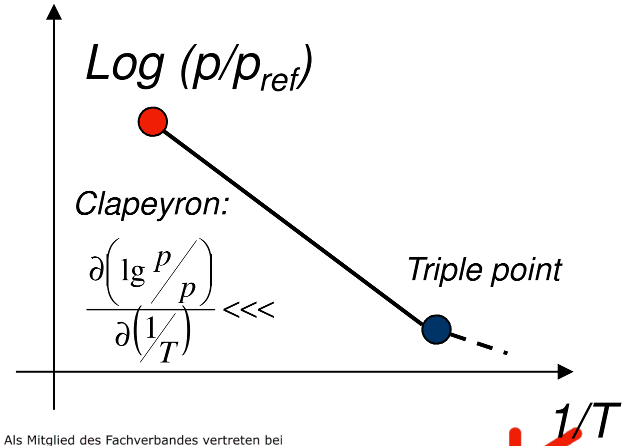
‚activity gas = activity solid‘

$$p_i = p_{total} \cdot y_i \cdot \varphi_i \big|_{gas} = p_i^* \cdot x_i \cdot \gamma_i \big|_{\text{solid condensed}}$$

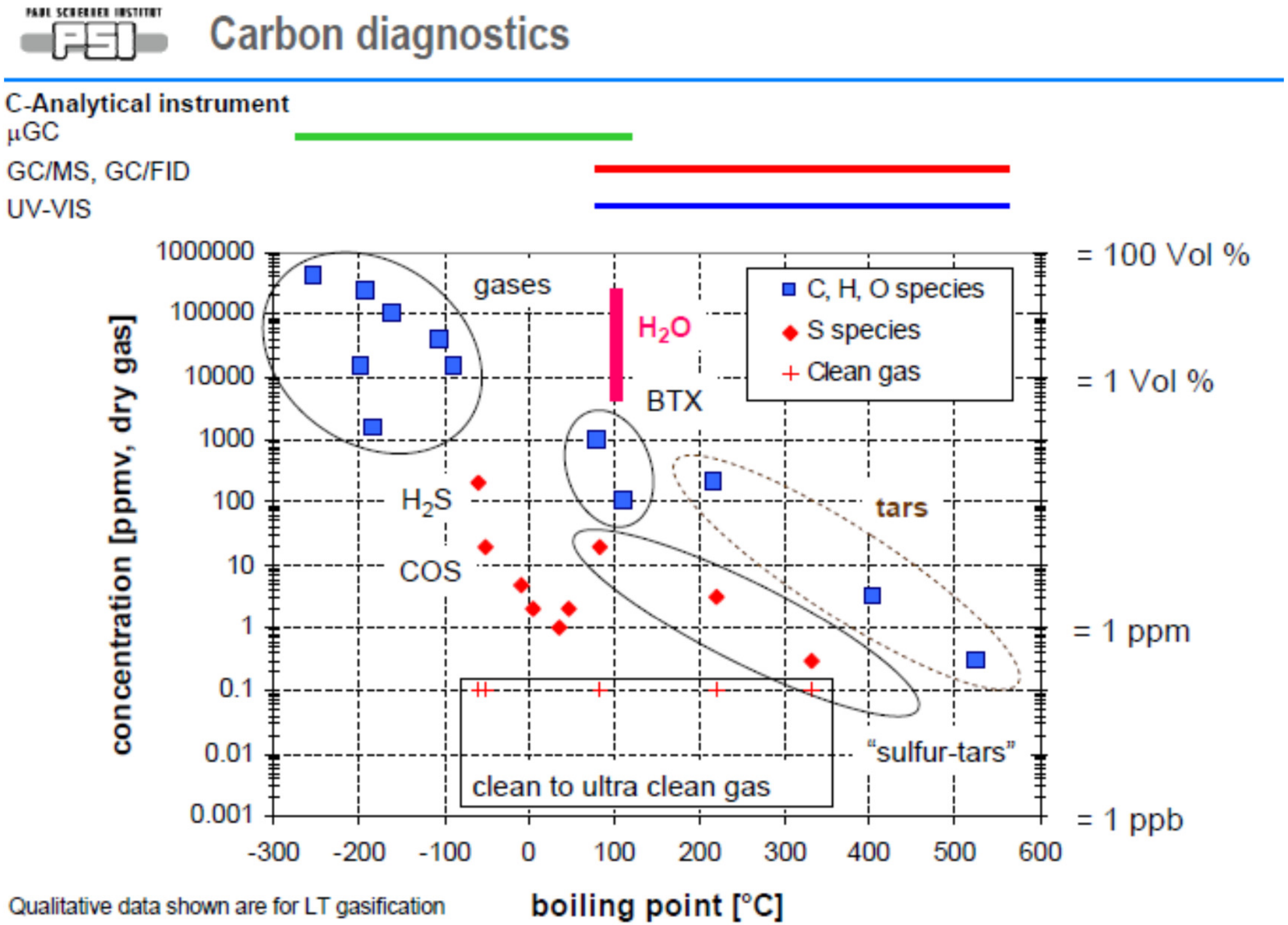
The clear and correct description of real substances is not as easy as it looks.
(serveral data ref.; missing data,..)

known in general





Physical fundamentals
data selection 'Tars', concentration mapping *S. Biollaz*



Qualitative data shown are for LT gasification

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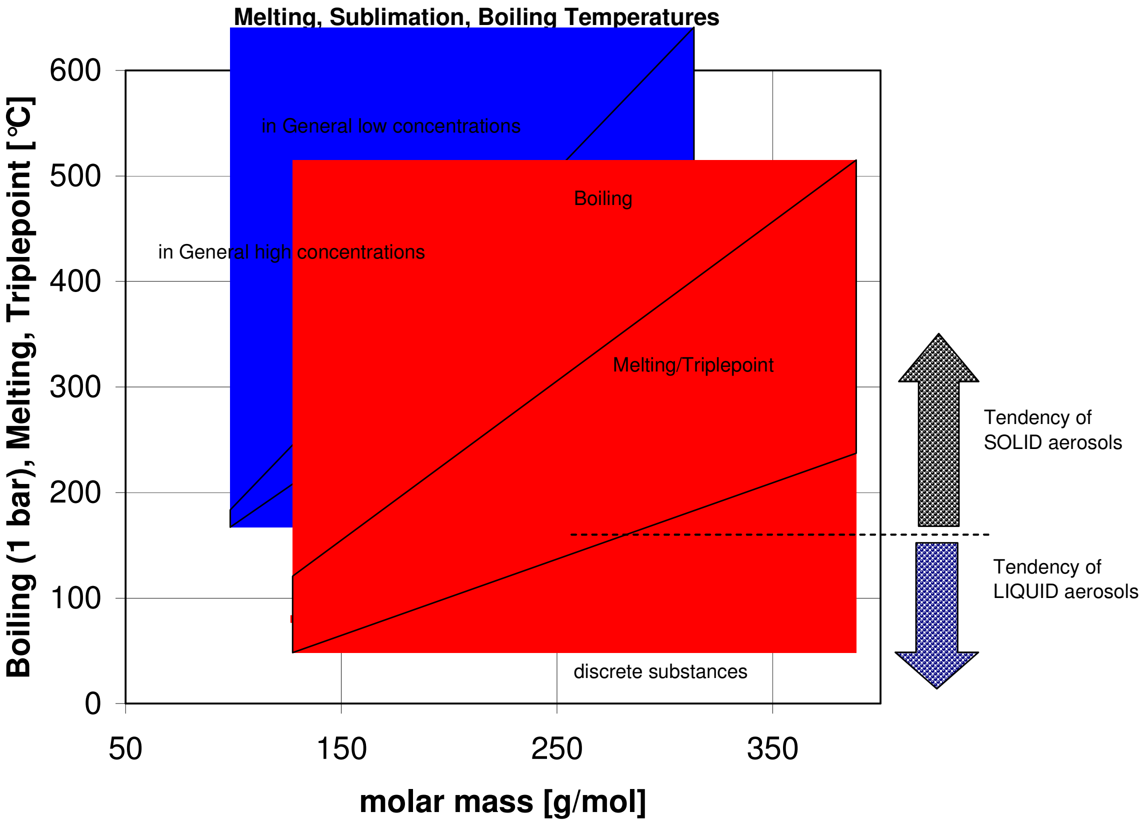
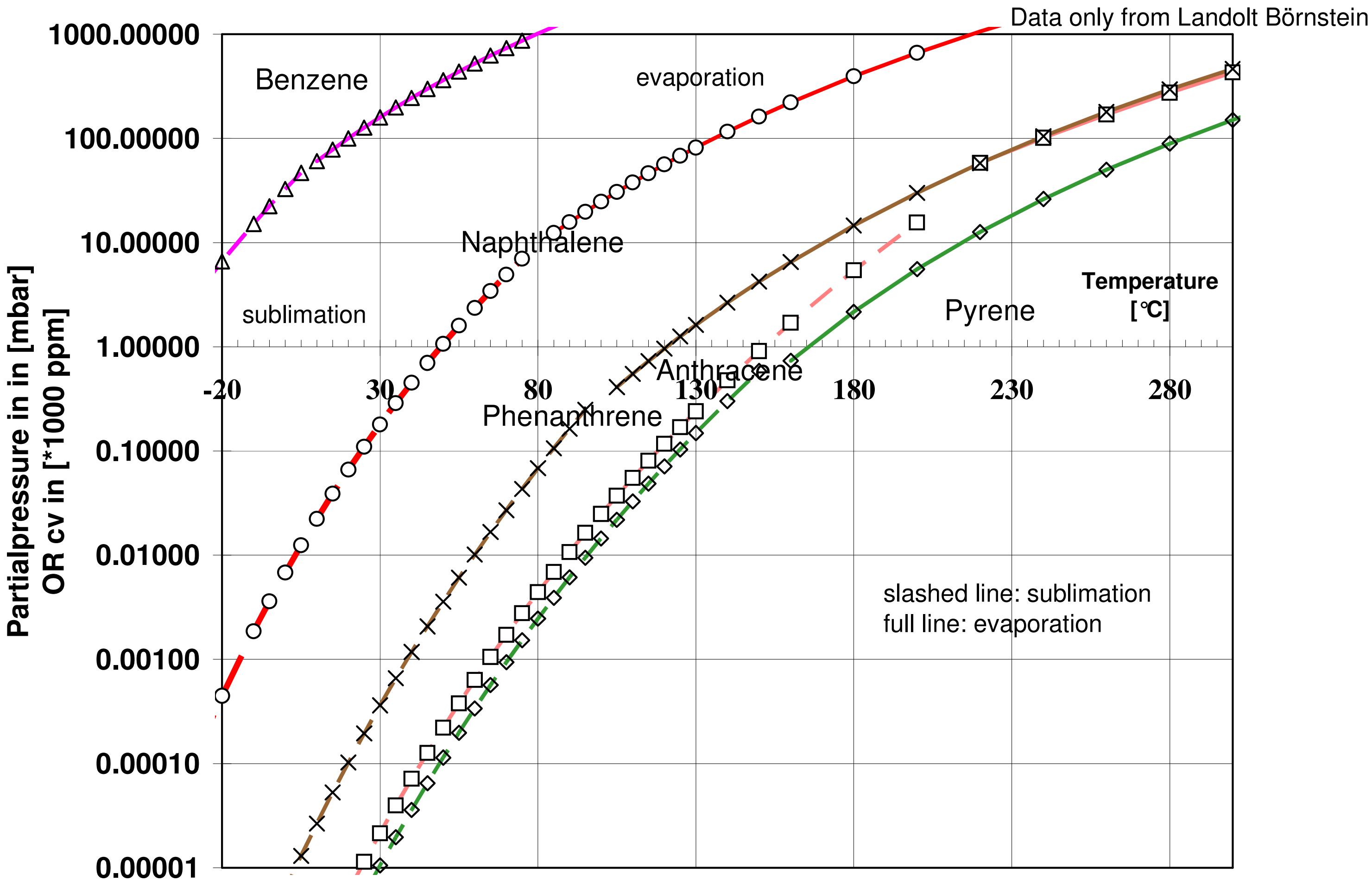
Physical fundamentals
data selection 'Tars'



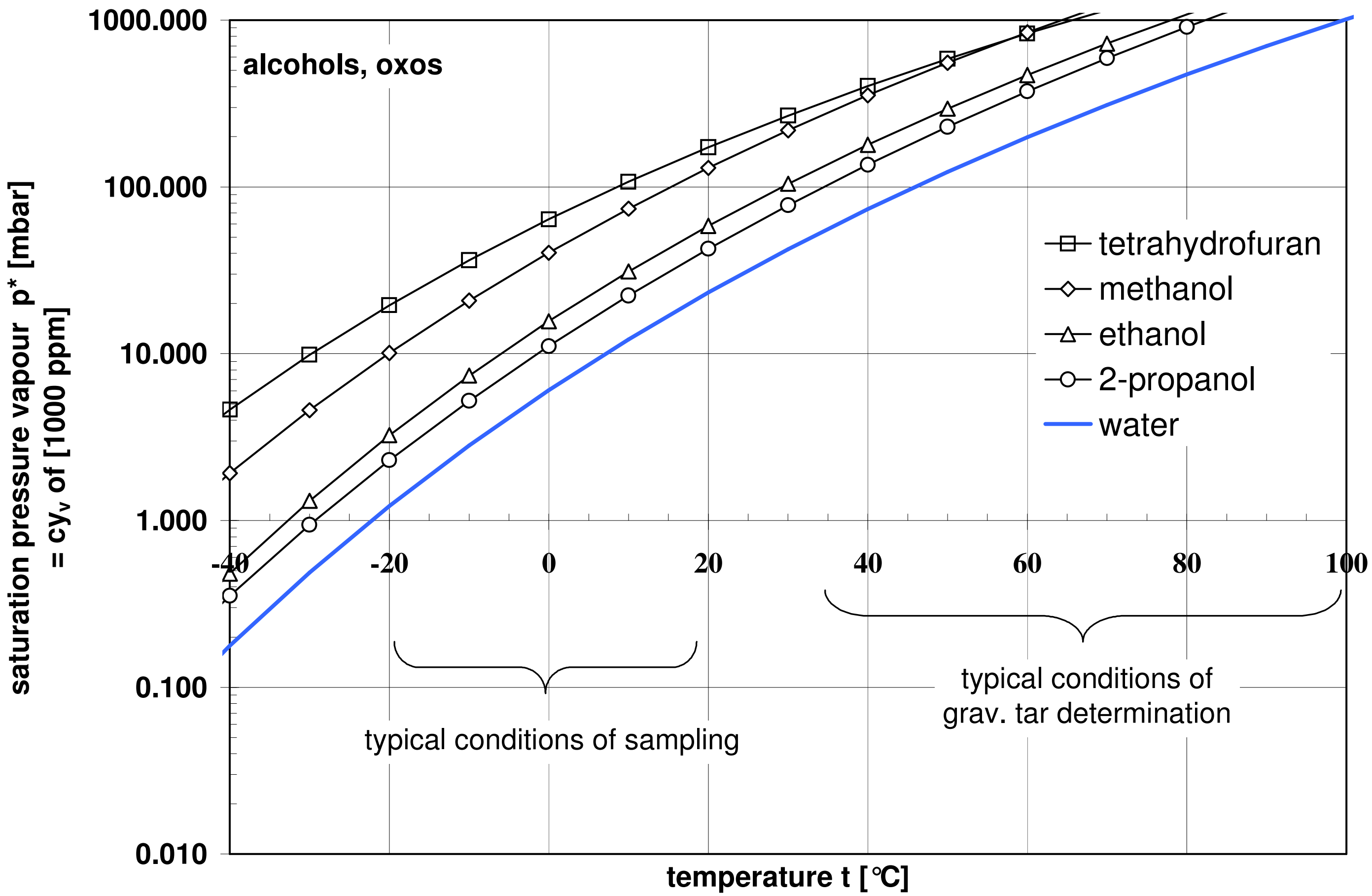
e.g. selection of PAH

		molar mass [g/mol]	boiling point [°C]	melting point [°C]
napthalene	C10H8	128.16	218	80
ace-napthalene	C12H8	152.2	275	93
acetyl-napthalene	C12H10	154.21	279	96
fluorene	C13H10	166.22	295	117
phenanthrene	C14H10	178.22	340	100
anthracene	C14H10	178.22	342	218
fluoranthrene	C16H10	202.26	393	110
pyrene	C16H10	202.26	404	156
a-phenylene anthracene	C18H12	228.29	435	159
chrysene	C18H12	228.29	448	256
b-phenylene-flouorene	C20H12	252.32	393	168
bk-f	C20H12	252.32	480	217
ba-p	C20H12	252.32	496	177
indeno(1,2,3,c,d)-pyrene	C22H12	276.34	534	162
di-benzo (a,h) anthracene	C22H14	278.35	535	262
benzo(g,h,l)perylene	C22H12	276.34	542	273

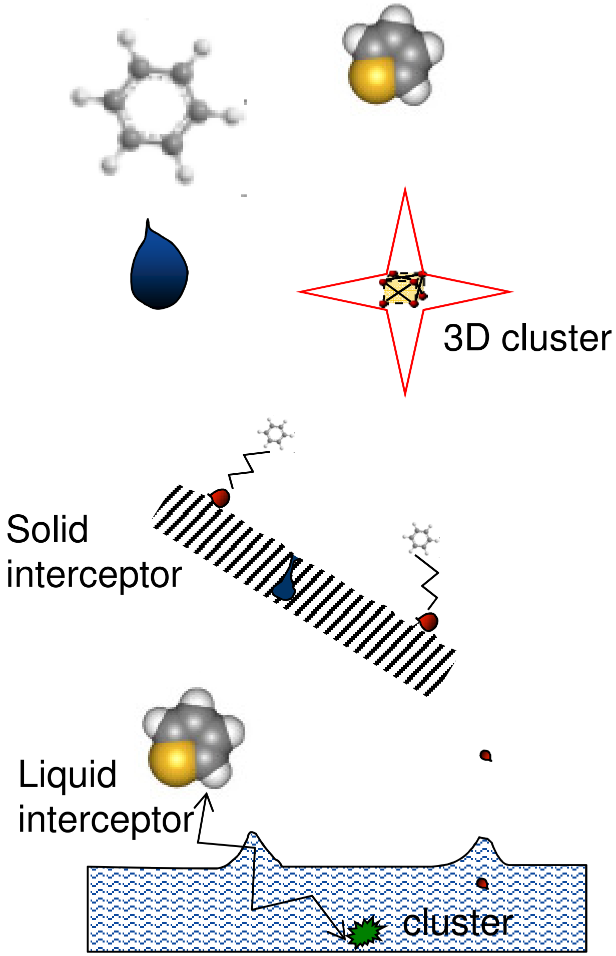
Physical fundamentals
saturation pressures of selected tars



Physical fundamentals
saturation pressures of selected solvents



Physical fundamentals
VLE of a selected tar against a solvent



VLE, VSE for a solution of compounds in solvents

Gas phase status, over-critical; sub-critical

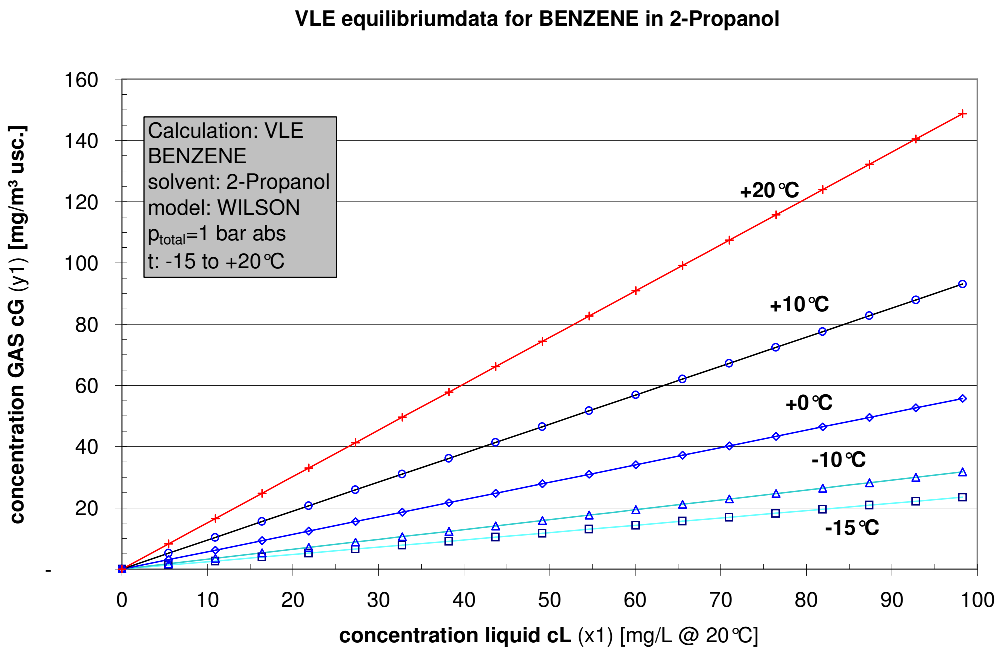
Formation of **droplets**: **Liquid** (condensation):
10^x molecules
Formation of **crystals**: **Solids** (re-sublimation):
in solid lattice

Adsorption: Energetically forced fixation
of clusters on surface, also pore / cavity condensation
div. mechanisms, degrees

Condensation: stable liquid phase

Absorption: VLE-Interaction into homogenous
liquid phase (solvent,..)

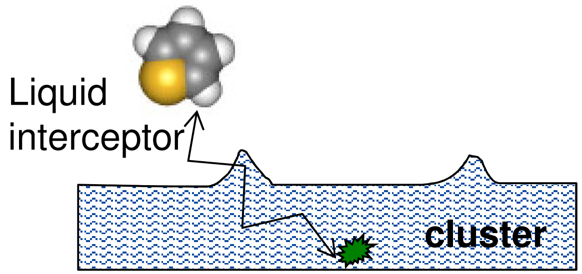
Physical fundamentals
VLE calculation and data support



In term of pressure:

A partial pressure below saturation can be reached,
because of homogeneous dissolution in liquid phase:
Law of Raoult.

e.g. when x_i <<<<!

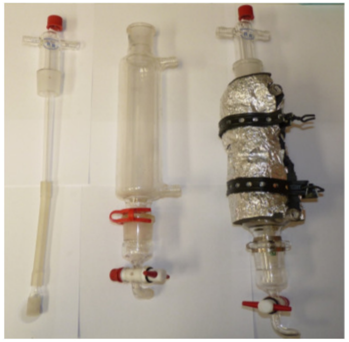


$$p_i = p_{total} \cdot y_i \cdot \varphi_i \Big|_{gas} = p_i^* \cdot x_i \cdot \gamma_{i,in\,\mathrm{solvent}} \Big|_{liquid}$$

Absorption: VLE-Interaction into homogenous liquid phase (solvent,..)

Test of a single stage accumulator technical outline

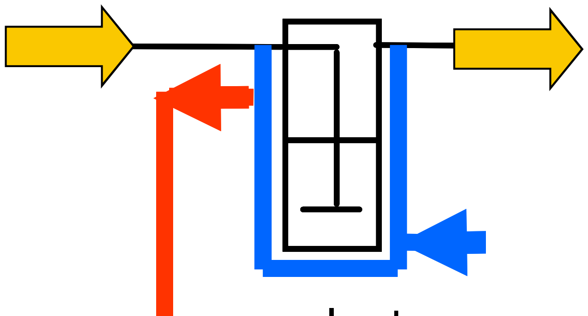
Reality



Balance-system

GAS in

GAS out



coolant

The **accumulation** is **instat. transient process**
Normally are impingers as **batch** operated.

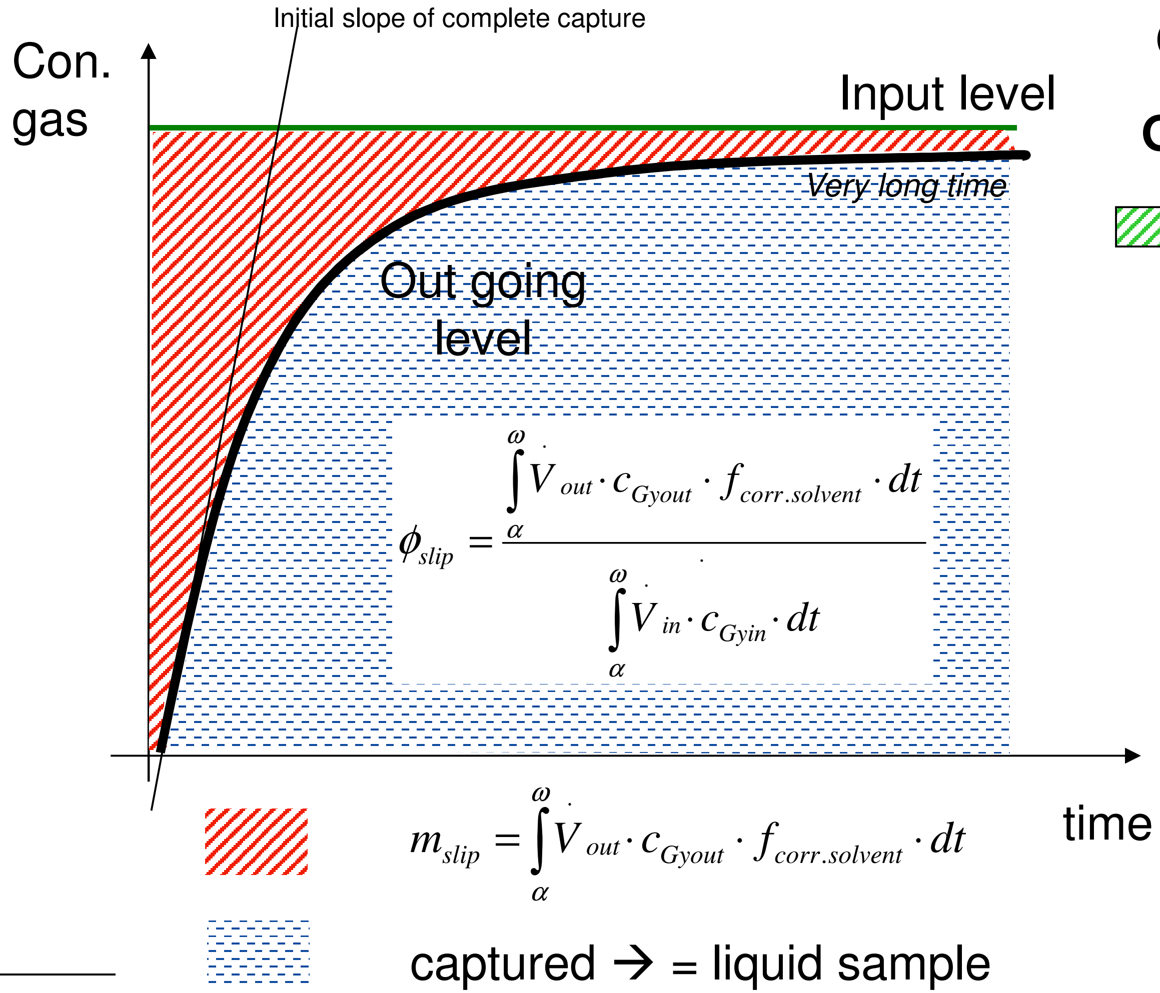
The capture depends:

- Ratio flow, capacity
- VLE
- Mass-transfer (condensation, interception,
- absorption, swarm of bubbles, contact time

For application important:

- Conditions of solvent
- Selectivity
- Multicomponents operation
- Capture in transient operation
- Suitable temperatures (VLE)
- Real aerosol capture

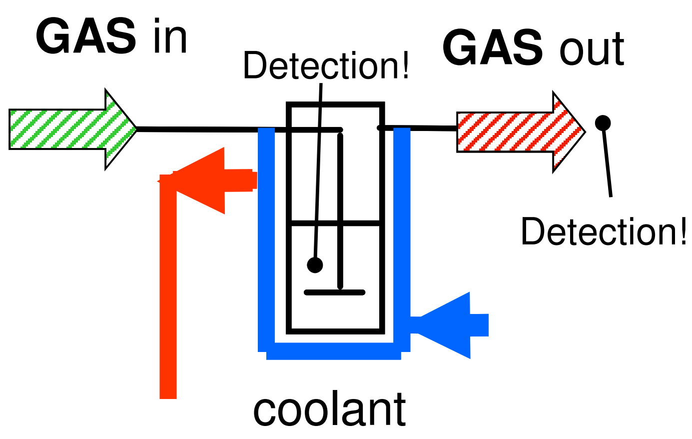
Test of a single stage accumulator: technical outline



$$\phi_{slip} = \frac{\int_{\alpha}^{\omega} \dot{V}_{out} \cdot c_{Gyout} \cdot f_{corr.solvent} \cdot dt}{\int_{\alpha}^{\omega} \dot{V}_{in} \cdot c_{Gyin} \cdot dt}$$

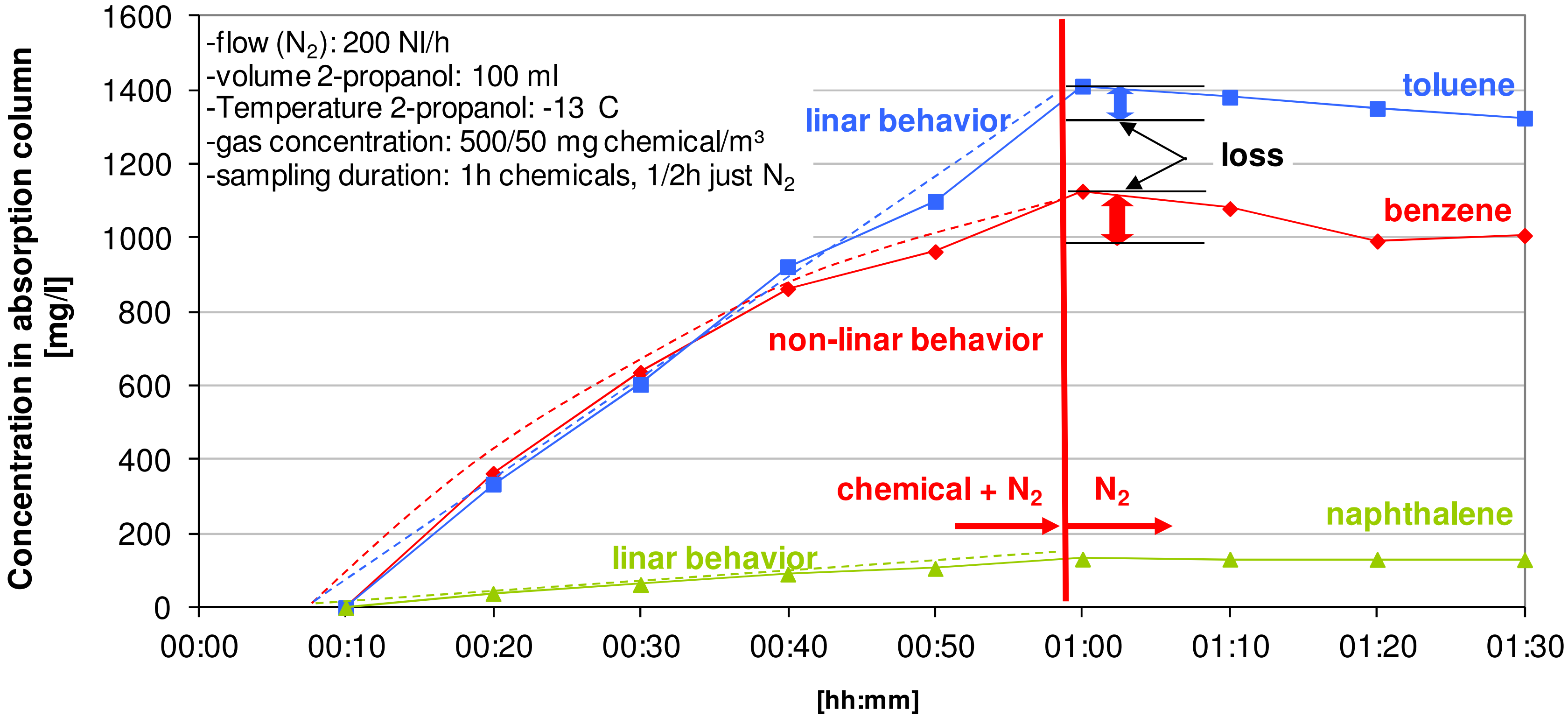
$$m_{slip} = \int_{\alpha}^{\omega} \dot{V}_{out} \cdot c_{Gyout} \cdot f_{corr.solvent} \cdot dt$$

Conditions of example:



- Constant flow of carrier gas
- Const. temperature
- Unchanged mechanisms
- Others (water, solvent)..

Test of a single stage accumulator results; 3 compounds



First period substance is within the carrier gas; then only carrier.

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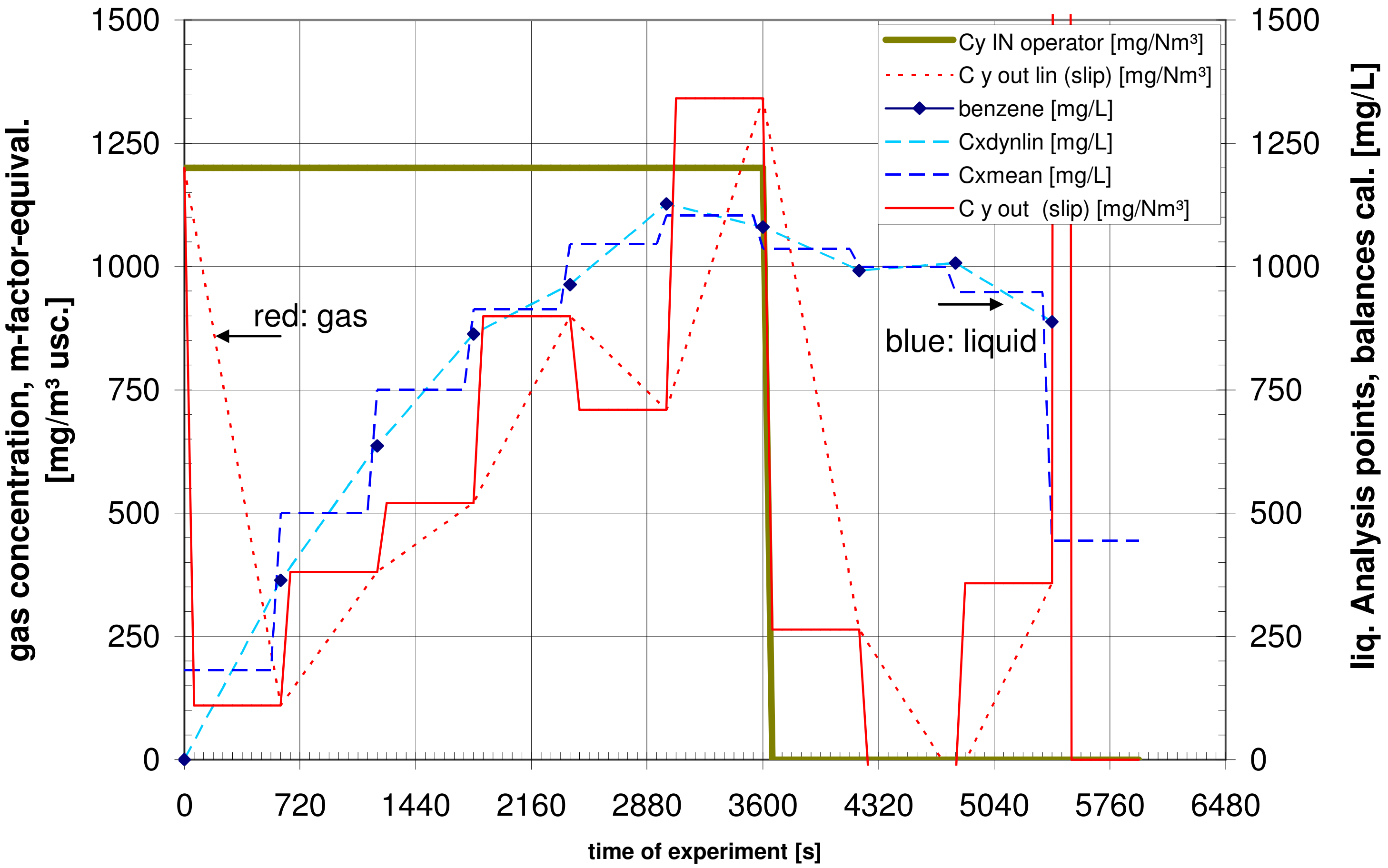
Test of a single stage accumulator results: dynamic *concentrations BENZENE*



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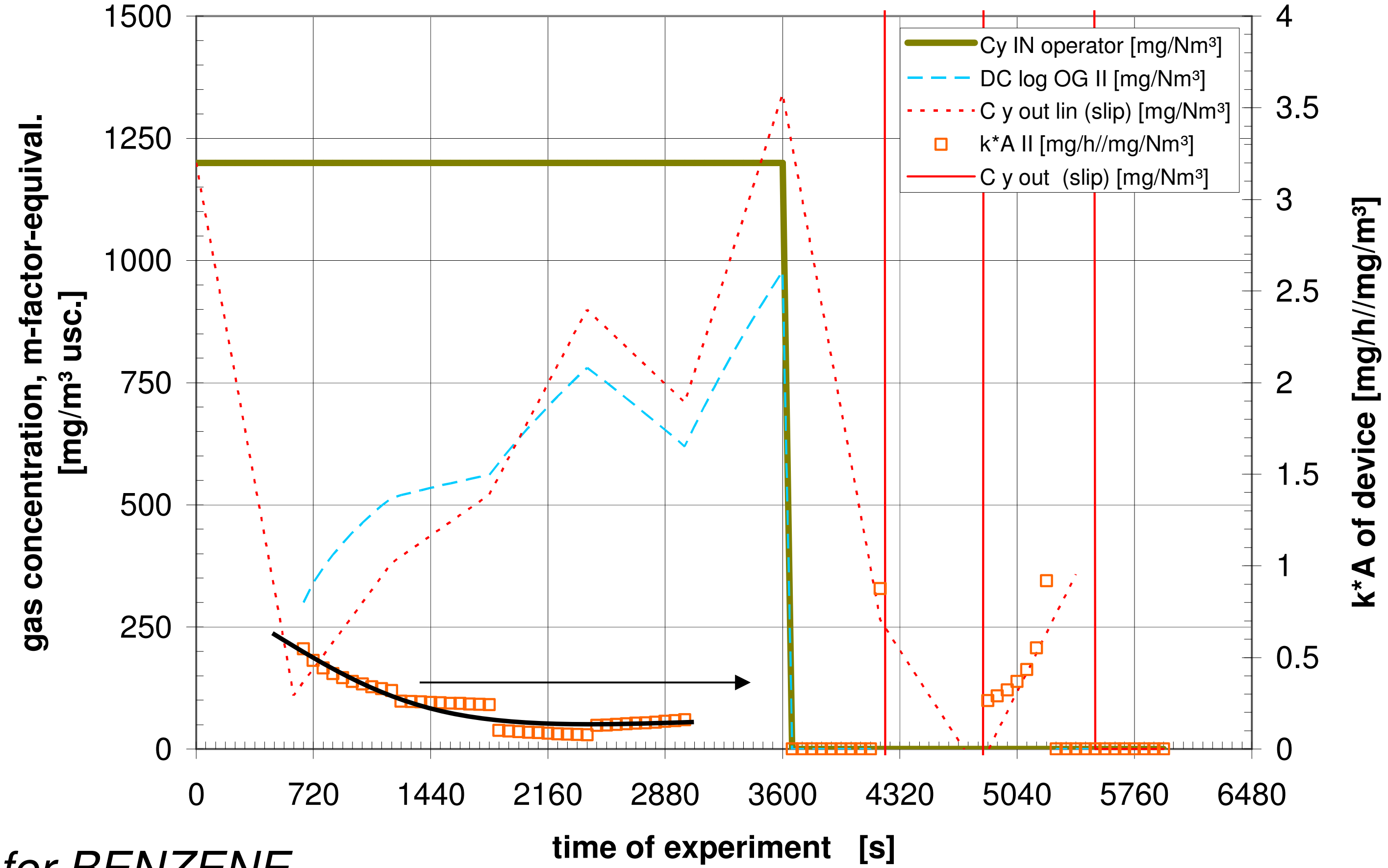
Test of a single stage accumulator results: *mass transfer-intensity: [k*A]*



specific for BENZENE