bioenergy2020+

‘tar protocol’ CEN / TS 15439

Status and next steps

Markus Kleinhappl Bioenergy2020+
Matti Reinikainen VTT

‘tar protocol’ CEN / TS 15439

13:00 h ‚technical part‘: *Markus Kleinhappl, Matti Rainikainen*

13:00-13:15: Long time experience of VTT

13:15-13: 45h (all) Strategy how a technological / scientific update might be made

Technological update:
- Sampling conditions
- Analytical conditions
- Quality measures

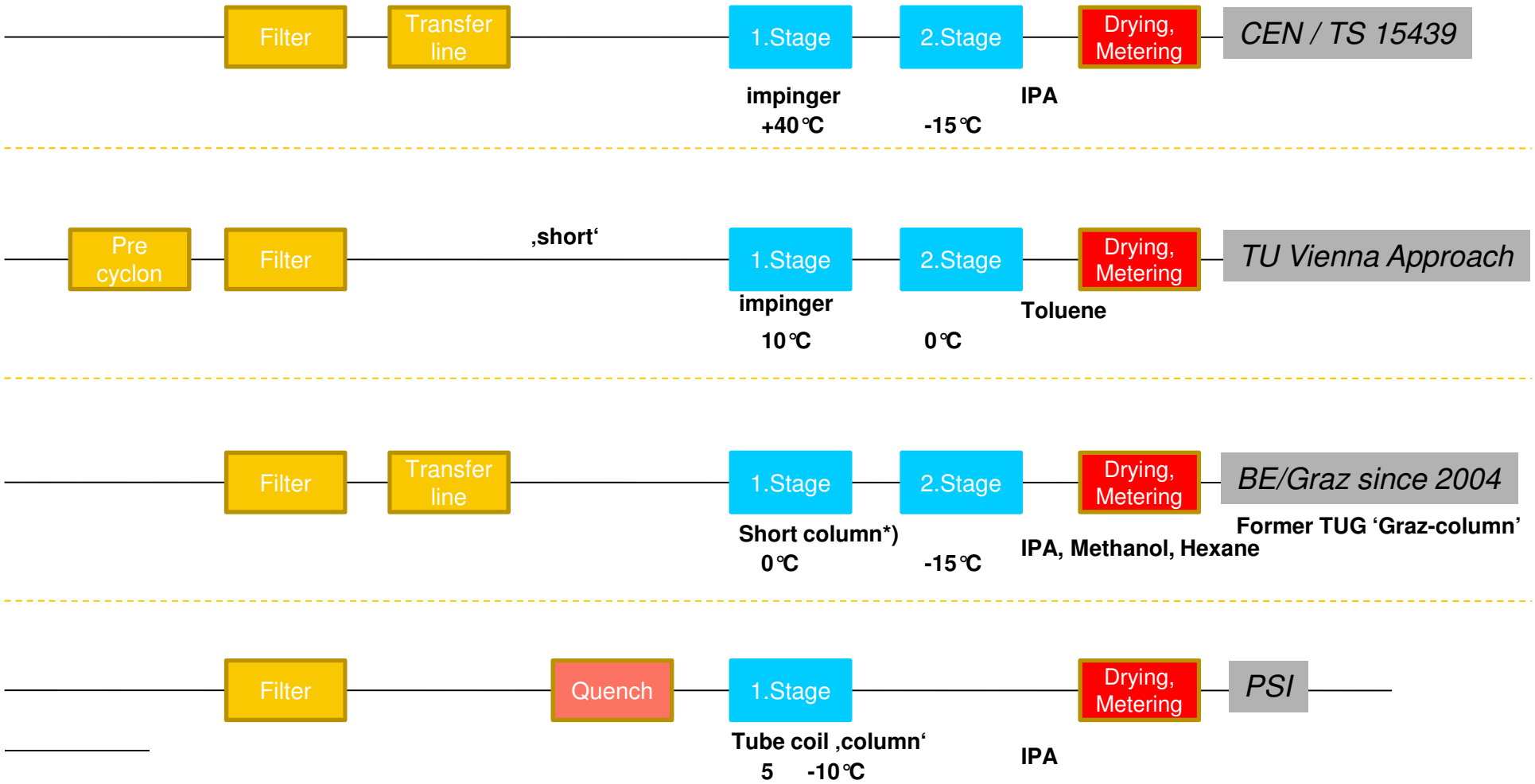
Scientific update:
- Statistics in quality measures
- Descriptors for sampling, capture, completeness
- Improvements distilled from round-robin

How to develop in future
What about fund raising

Technological update

- Derivatives of the CEN/TS 15439
  How it is applied
- Interaction: gas type and target of measurement
- Detection conditions
- Detection effects

Suitable Concepts ‘derivatives of CEN / TS 15439



‚bio-diversity‘ of applications with good experience.

Sampling parameter, Conditions, Range

Particle ***Aerosol*** ***Tar***	Gas family	Sampling conditions	Relative Gas volume V_{Gas}/V_{Liquid}	Range of detection

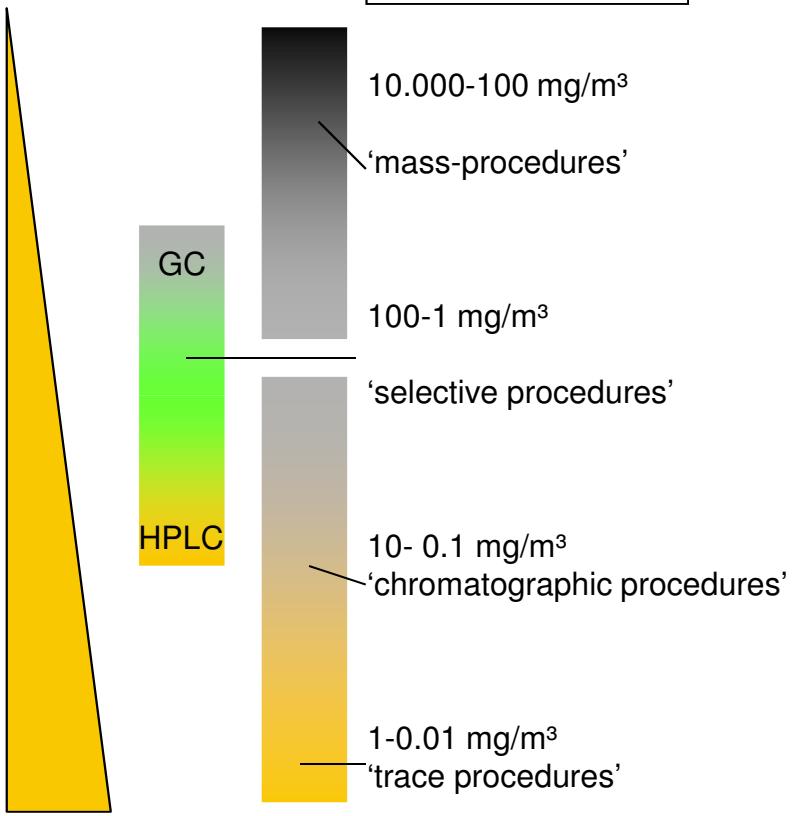
Particulate
Tar for grav.
Tar for HPLC
Tar for GC
Tar similar comp.

Pyrolysis
Torrefaction.
Counter current gasifiers
Fluidized bed gasifiers
Entrained flow gasifiers
Co-current gasifiers
Staged gasification
Treated product gas
Treated synthesis gas
Flue gas

Crude Gas
High dust
High tar
High water
High temperature
Pressure

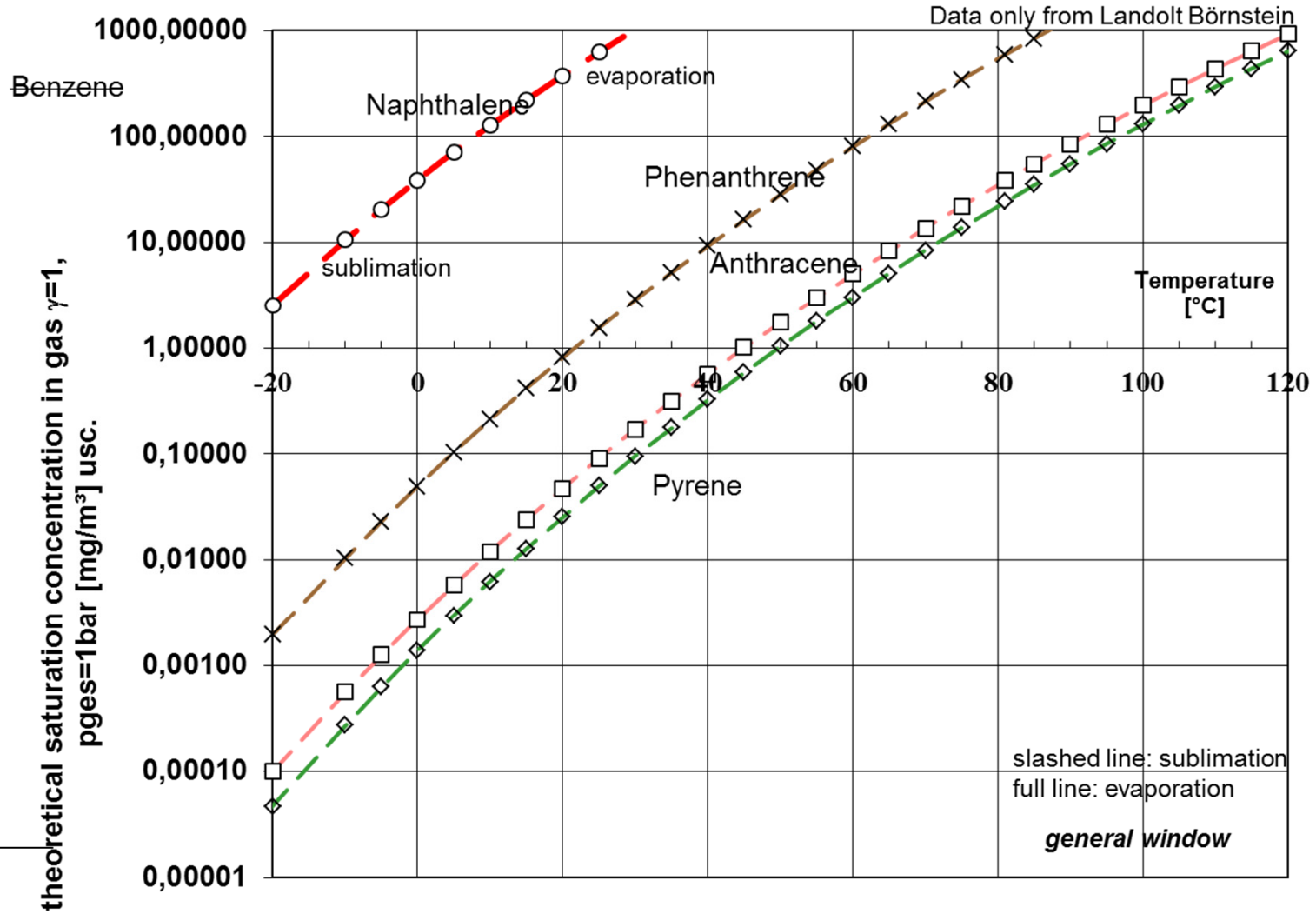
Treated gas
Medium dust
Medium tar
Medium water
Medium temperature

Finished gas
Low dust
Low tar
Low water
Ambient temperature
Very high pressure

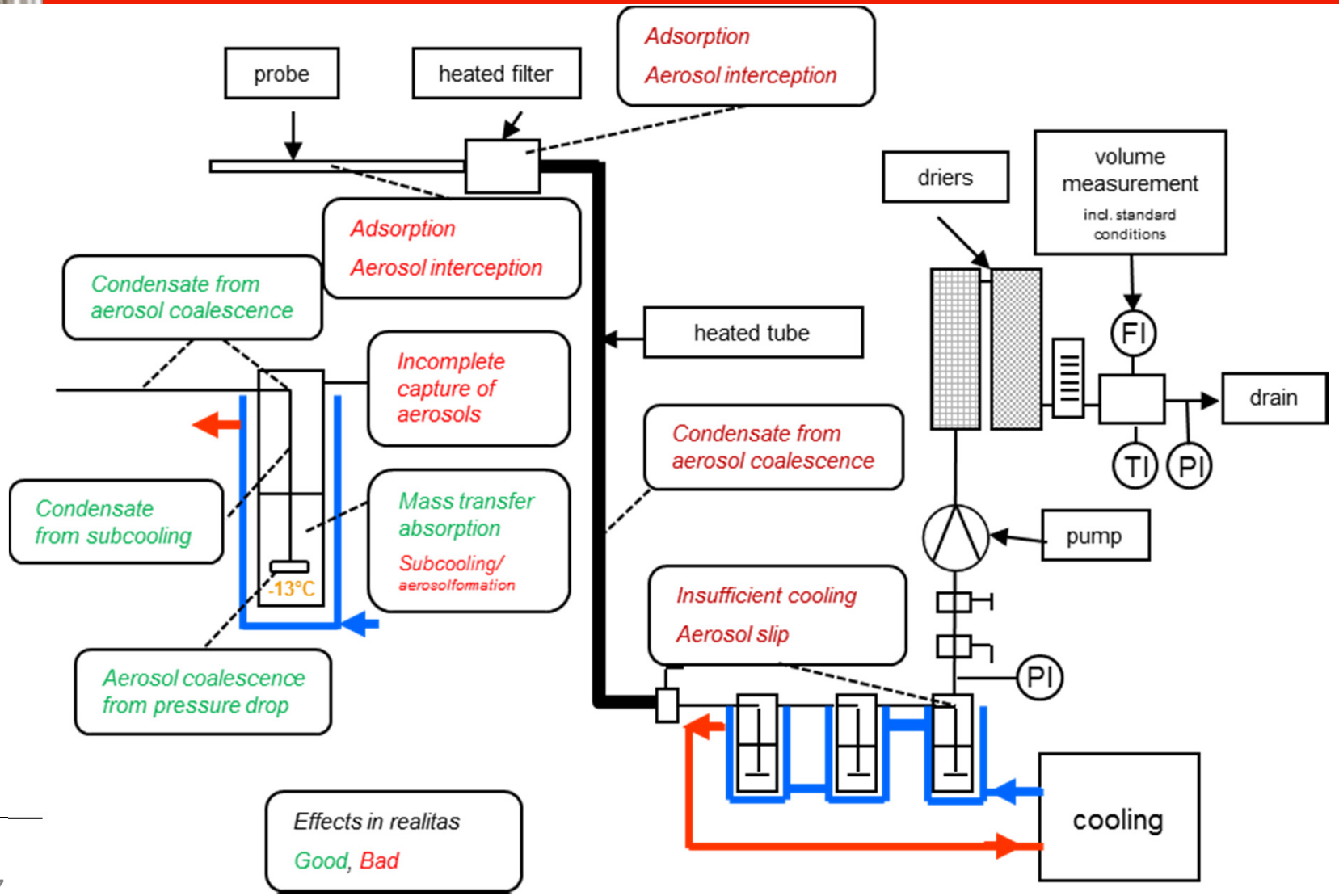


Interface connector: sampling-analysis combination

Primitive fundamental = basic value
Saturation pressures/ concentrations

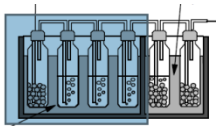


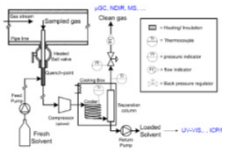
Effects all over the sampling line



Sampling parameter, Conditions, Range

Sampling conditions	Relative Gas volume V_{Gas}/V_{Liquid}		Mass of analyte desired	Range of detection
	Relative capture		mg total of each	
Crude Gas				
High dust	0,1 m³G/250 ml L		200-1.000 mg	10.000-100 mg/m³
High tar				
High water	0,1 m³G/100 ml L			‘mass-procedures’
High temperature			1-50 mg	
Pressure	0,25 m³G/100 ml L			100-1 mg/m³
Treated gas				
Medium dust			0,5-10 mg in 100 ml	‘selective procedures’
Medium tar	0,5 m³G/100 ml L			
Medium water			0,05-1 mg in 10 ml	
Medium temperature	1,0 m³G/100 ml L			
correctly			1-5 ng [C] as limit of FID Total: (x100)	10- 0.1 mg/m³ ‘chromatographic proc
Finished gas	1,0 m³G/100 ml L	10 ml L		
Low dust			1-50 µg/l Fluorescence	
Low tar				
incorrectly				
Low water	1,0 m³G/100 ml L	5 ml L		
Ambient temperature			Enrichment: SPE (sampling)	1-0.01 mg/m³ ‘trace procedures’
Very high pressure	5,0 m³G/100 ml L	5 ml L		
			SPE-extraction in sample fractioning (PAH, PASH, BTXE,..)	



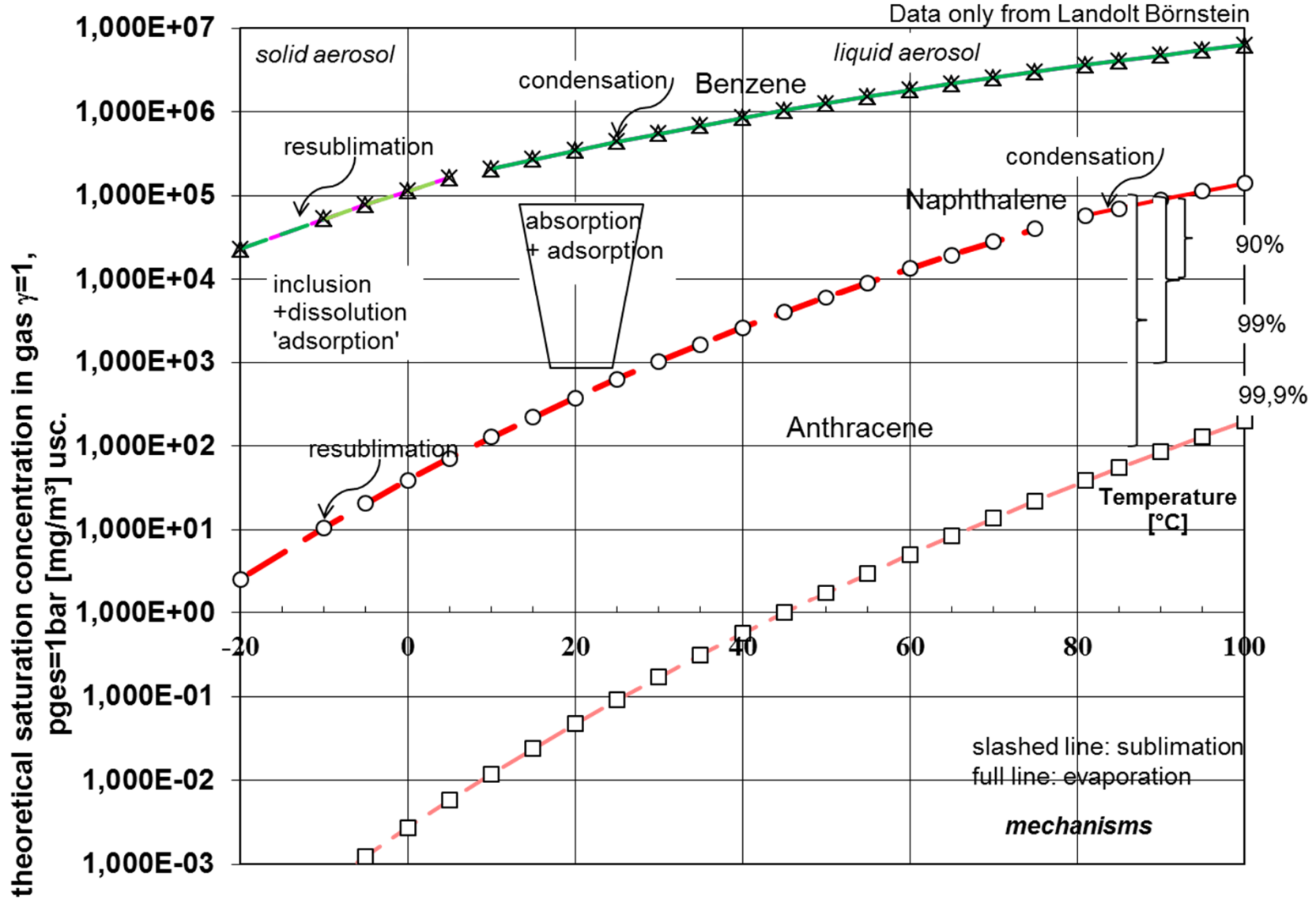


GC

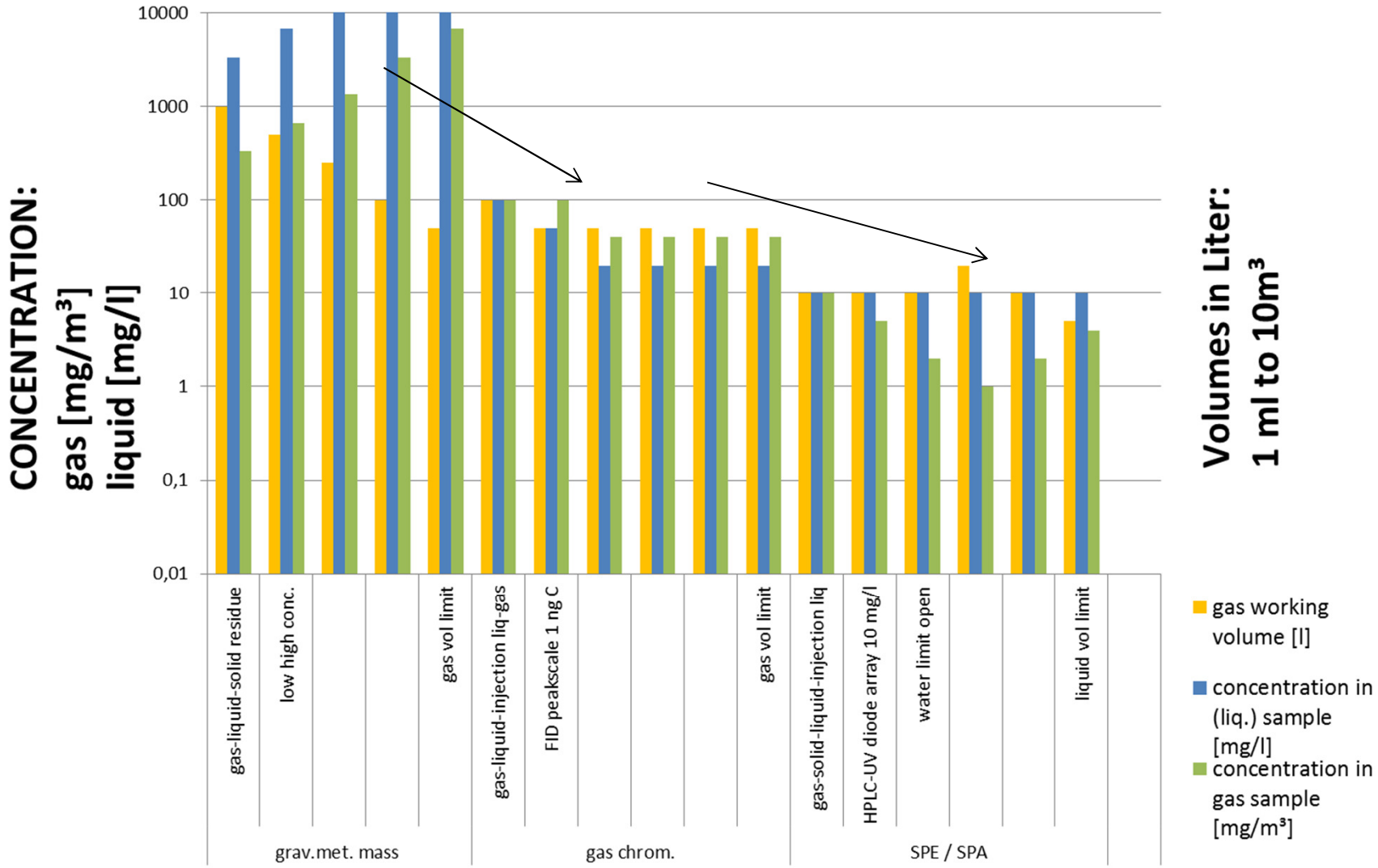
HPLC

Sampling must be better in 1-degree complete than the Analysis is operated.

Completness of capture: 90% 1 magnitude; 99% 2magnitudes



The gas/liquid ratio limits of quantification: *lower limits*



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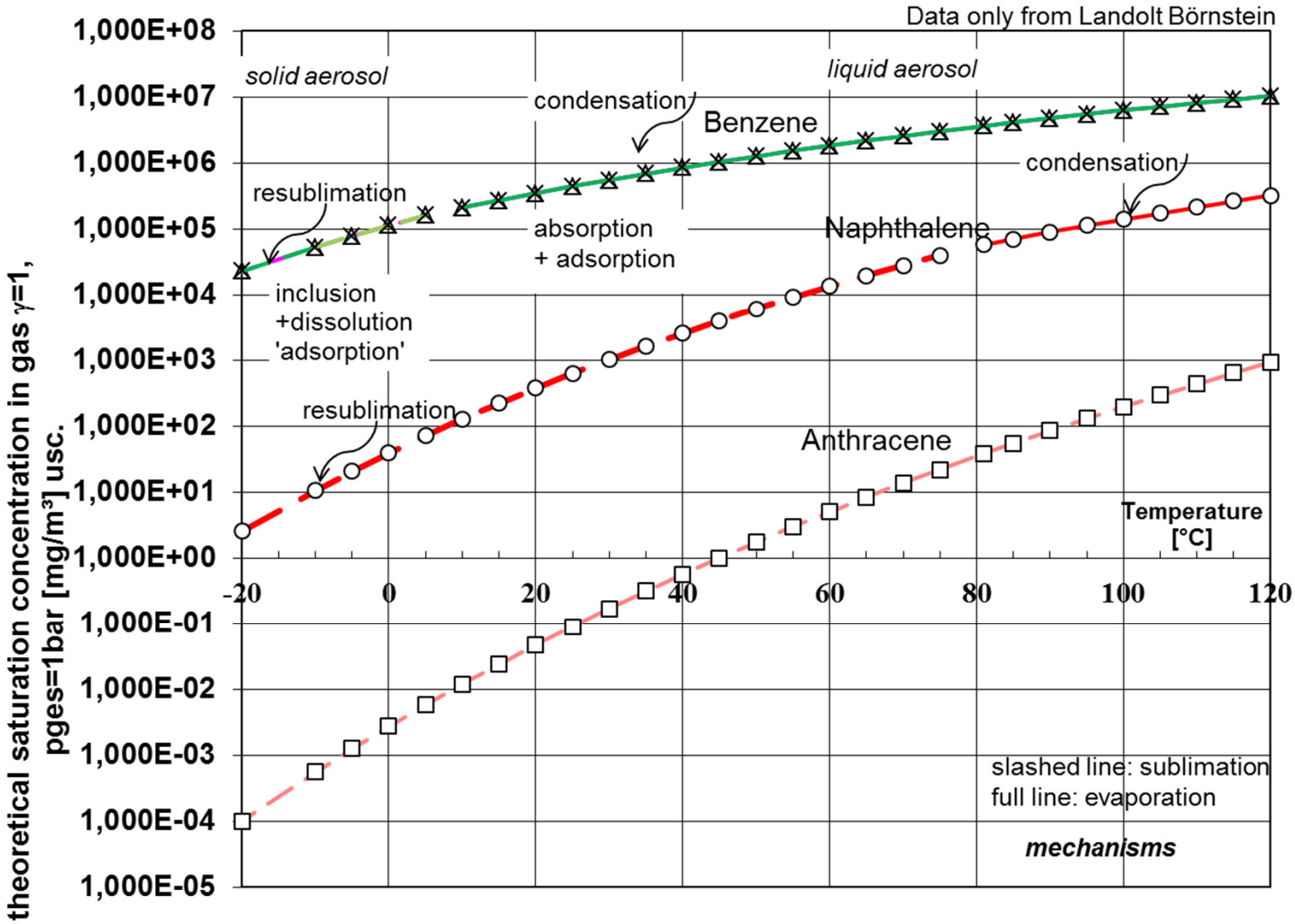
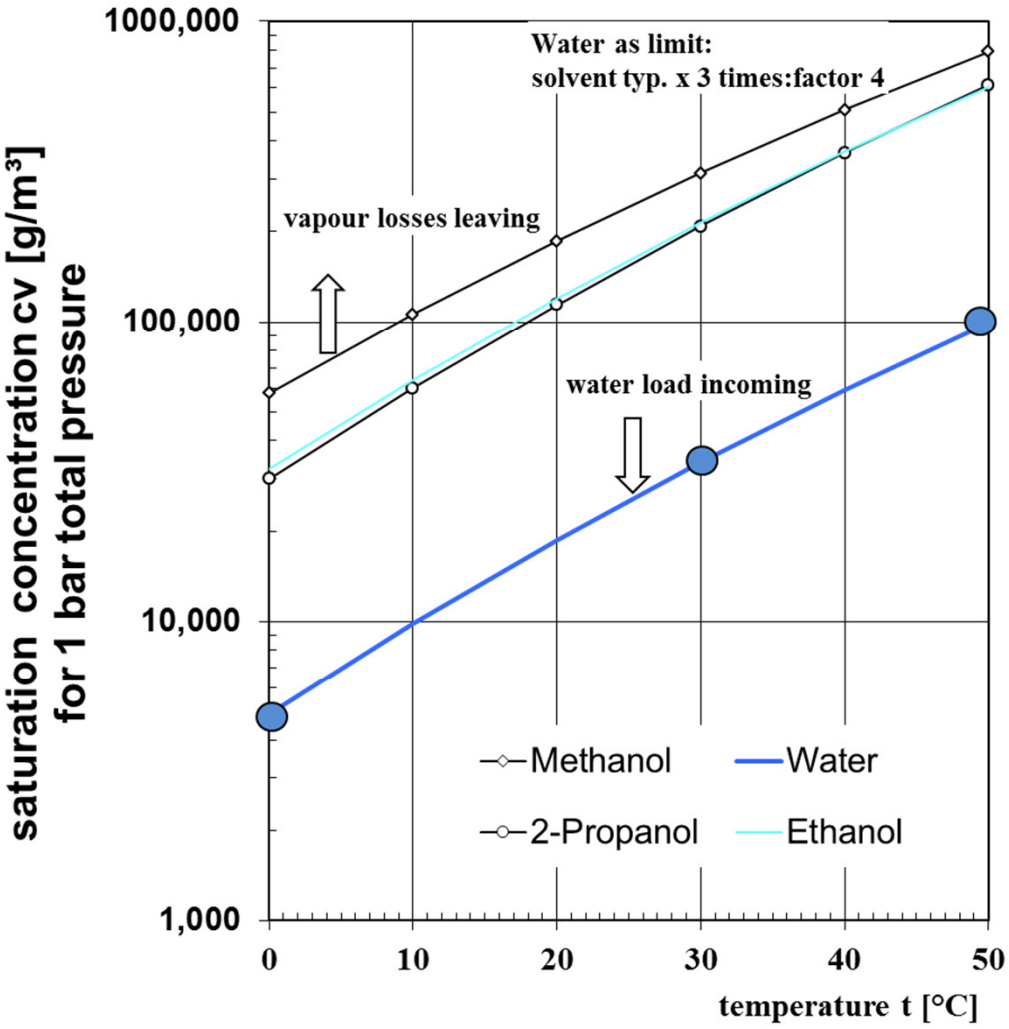
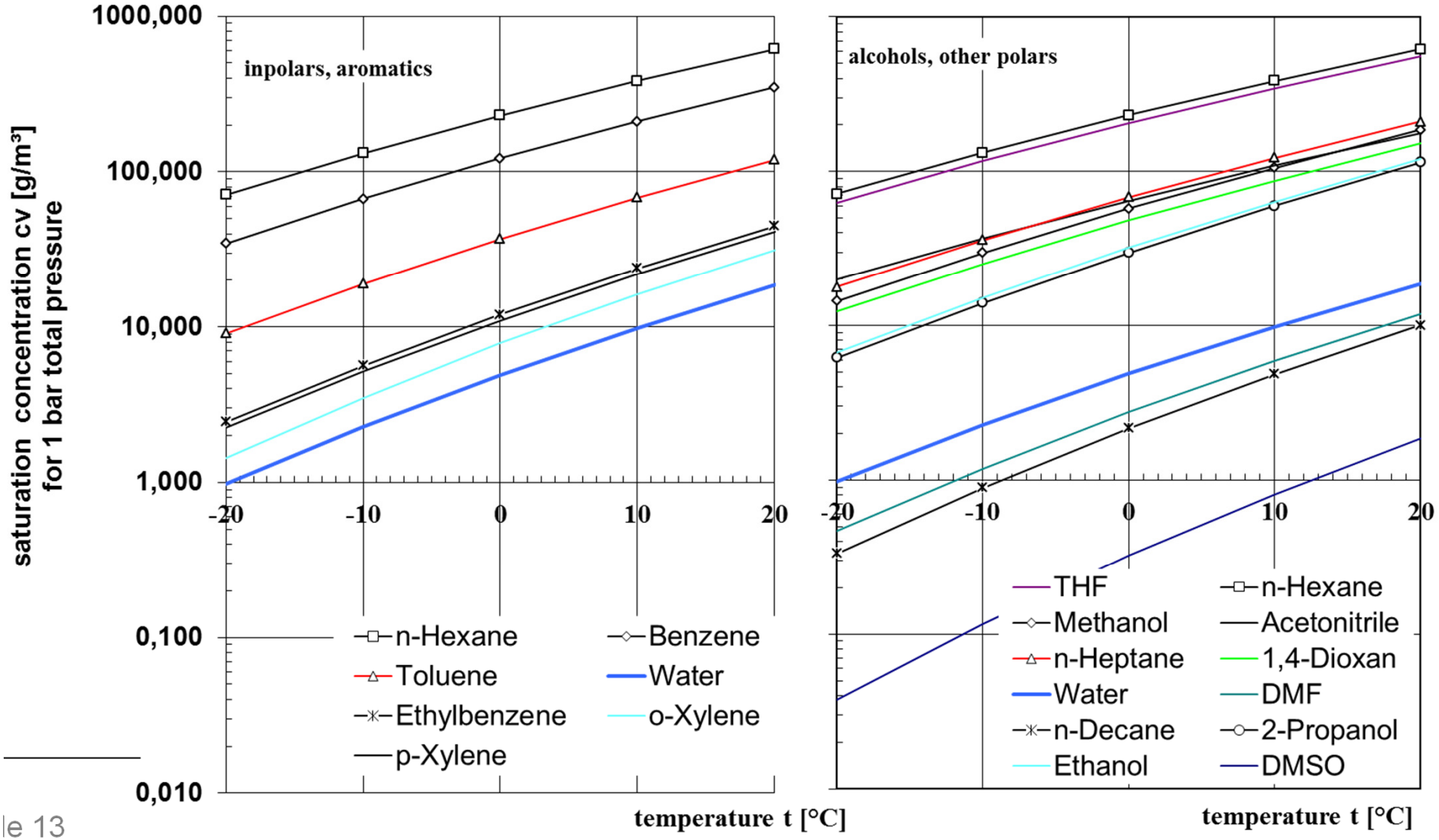


The water problem in liquid acc. sampling



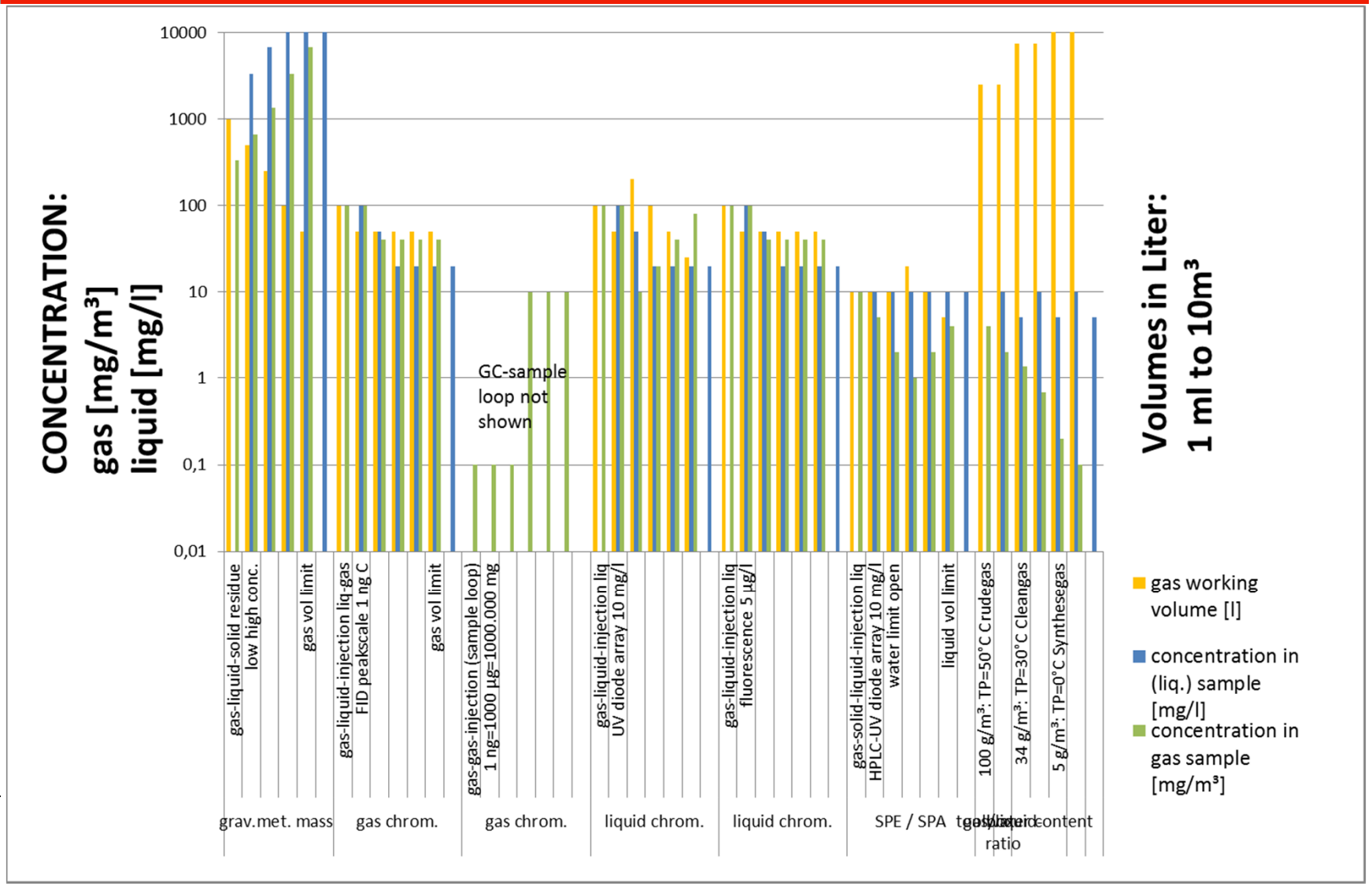
The selection of solvents: saturation-losses



Scientific update: back ground

- Mechanisms during sampling
- E.g. equilibrium effects during sampling
- Mass transfer for accumulative (glas-) equipment
- Improvement of procedure description
- Targets can be expected
- Better approach for quality measures (effects, capture + sampling conditions)
- Extend the title of the CEN/TS from: TAR organic compounds (targets of gases changed)

The gas/liquid ratio



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Tar for HPLC

Tar for GC

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Co-current gasifiers

Staged gasification

Treated product gas

Treated synthesis gas

Flue gas

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Finished gas
Low dust
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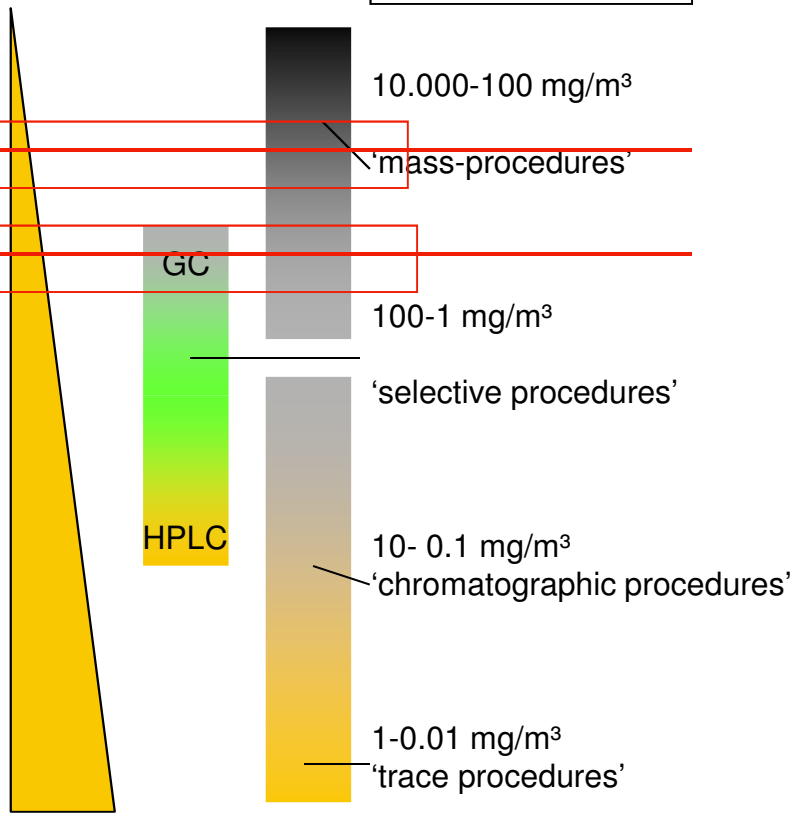
Ambient temperature
Very high pressure



10.000-100 mg/m³
'mass-procedures'

100-1 mg/m³
'selective procedures'

10- 0.1 mg/m³
'chromatographic procedures'

1-0.01 mg/m³
'trace procedures'

Sampling parameter, Conditions, Range

Sampling conditions

Crude Gas
High dust
High tar
High water
High temperature
Pressure

Treated gas
Medium dust
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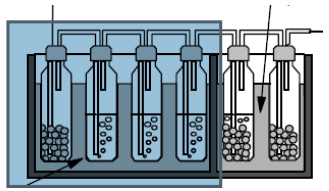
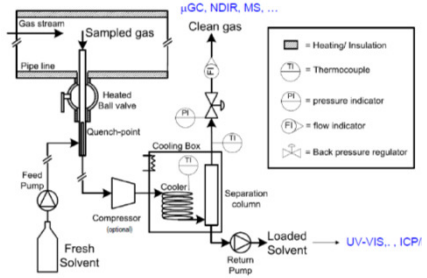
Finished gas
Low dust
Low tar
Low water
Ambient temperature
Very high pressure

Relative Gas volume
V_{Gas}/V_{Liquid}

Relative capture





Range of detection

GC

HPLC

10.000-100 mg/m³
'mass-procedures'

100-1 mg/m³
'selective procedures'

10- 0.1 mg/m³
'chromatographic procedures'

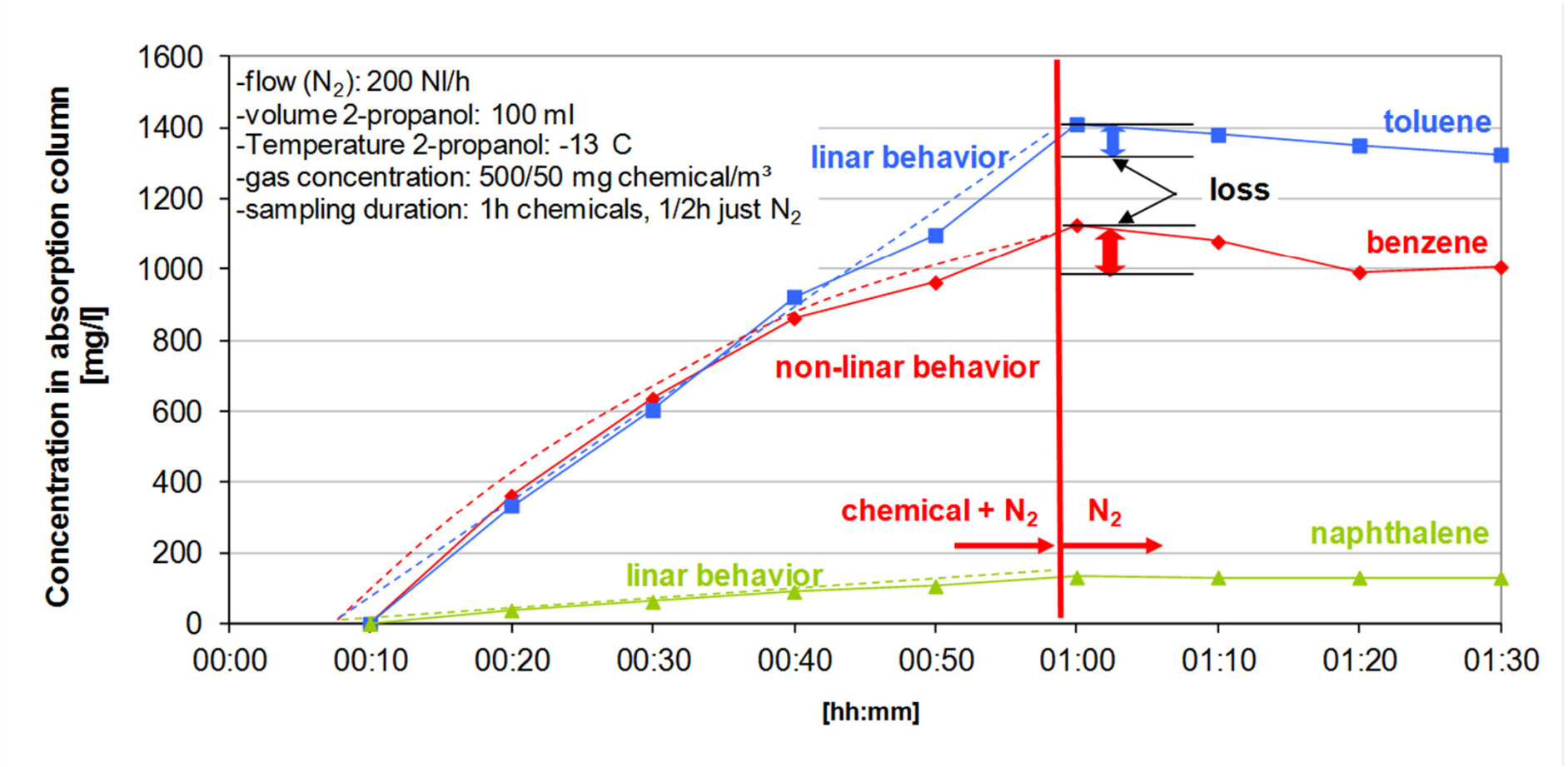
1-0.01 mg/m³
'trace procedures'

correctly

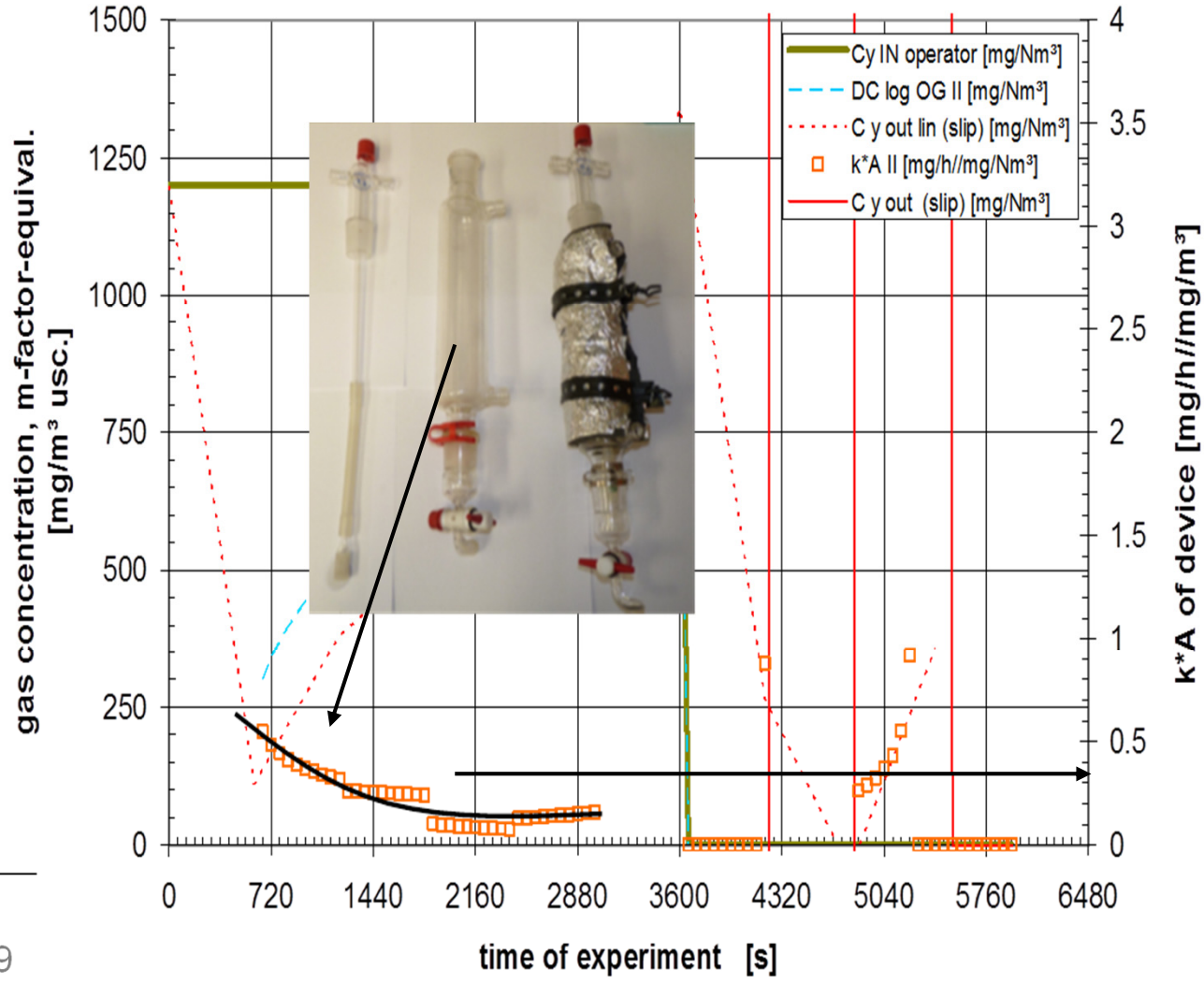
incorrectly

In General: Sampling must be **more complete** than the Analysis **can see.**

The dynamic sampling performance of an impinger system 1



The dynamic sampling performance of an impinger system 2



Sampling parameter, Conditions, Range Postulates

The complete sampling procedure (gas extraction, prefilters T1, accumulation T2) must be suitable for:
Absolute concentration of analyte, relative amount of compound lightest heaviest,
completeness in capture, minimal amount of compound.

Sampling drain T1, T2 must guarantee **completeness** under conditions: Flow rate, water content, **target temperature** of T2, combinative problems (dilution with water, ice formation).

Sampling must be better in 1-degree complete than the analysis is operated.
e.q. slip should be lower than 5% of income.

In general ONE sampling condition (T1+T2) can't guarantee the capture of all ‚classes' desired.

Physical limits of: equilibrium, solubility, capacity, mass-transfer (=capture ability) should be respected on scientific-technological level.

Recommended procedures: deliver **reproducibility**, **repeatability** and **reliability**.

Performance is evaluated in RR in 3 stages (degree of effort, ,..).

Next steps

- Your feedback
- Webinar-group about the UPDATE of CEN/TS
- Legal conditions and procedure for edition of a CEN/TS
- Outcomes of the round robin (results from each host site versus institution's approach)
- Update process

Which items can be updated to CEN /TS?

Improvement of definitions/declarations

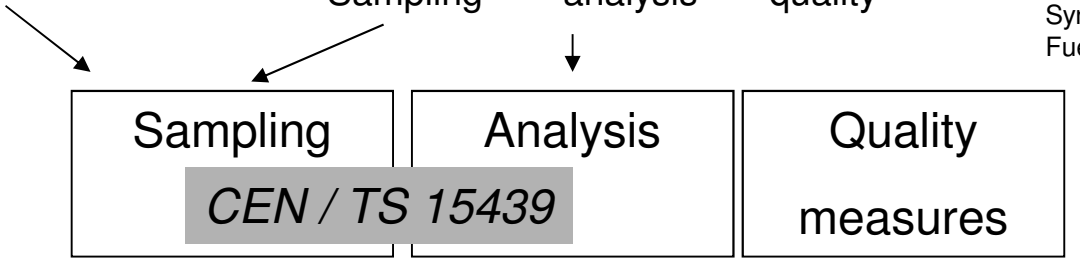
/ **Type of Gas**
/ **Degree of Treatment**

Pyrolysis
Types of Gasifiers
Productgas for Engine
Syngasconversion
Fuelcells

/ **discrete Components**
/ **families of compounds (=classes)**
/ **physically lumbed classes**
Methodology of
Sampling analysis quality

/ **Utilisation target**
/ **specific recommendations**

Gas for:
Burners
Engines
Syngasconversion
Fuelcells



/ Cluster of quality parameters
Particulate
Aerosol matter
'tar'
'tar-species'
Other
Include/exclude PASH

Introduction of new technology crosslinks

News:
Filter – elements /cross flow/ dilution methods
Sampling probes (heated)
Particles/aerosols/ classification of solids (on temp.)
Impingers columns cont. masstransfer
Liquid methods SPE (solid phase)

News:
Offline/online
detection/measurement
HPLC/GC-methods
Selective Recovery from SPE
Hyper-systems with toolboxes®
Waterdetection

Test procedures of capture & analysis (testgas generators)

News:
Reference method approach:
Target physical conditions (effects)
method reliability
method approach
Target
Round Robin I / II / III
Test procedures

Item quantified: method specified equipment recommended (=procedure selected)

How to get a result?

CEN / TS 15439

Quality measures

Sampling conditions → Sampling → Analysis → Result target

Equipment has to accept the conditions

Which approach?

Equipment

Procedure

Equipment is suitable for ……

Structure of CEN/TS ‚guideline'

Scale Range:
1000
100
10
1
0.1
0.01
0.001

Systematic test of methods approach for target recommended: wheel of workflow…..

Codex:
Used for.....

Works as reliable standard....

Useful for comparison.....

physical conditions (effects) classified (e.g. equilibrium status, capacity of capture,..), masstransfer

Forecast of method' improvement

New item:
1…..
2…..
3…….

Starting point:
Future target

Test of reliability / reproducibility / repeatability

Round Robin I / II / III
Test procedures

Host 1
Host 2
Host 5
Host 3
Host 4

Recommended approach

CEN / TS 15 439

Update
Related documents

Update or appendix of CEN

Sampling	Analysis	Quality measures
CEN / TS 15439		

Systematic extension of CEN / TS 15 439: appendix, related documents

Sampling	Analysis	Quality measures
CEN / TS 15439		

CEN / TS 15 439
Core document

Definitions
Targets to be sampled
Central-Method

CEN / TS 15 439
Appendix

Glossary
Parameter charts (Limits)
Procedures
Equipment, similar approaches
Quality measures
Comparative results from RR

CEN / TS 15 439
Related documents

Sampling of other substances ‘tar-like’
Common interface for chem. Parameters

Detailed results of RR-tests

Extent the application from tar to organic compounds

(Gas-)Quality = fulfilment of limits defined ‘Parameter-stamp’ = maximal extended chart….

Type of **parameter**	**Physical defined limits** **Physically constituted**		**Chemically or of constitution clear defined**	
	Dew point (of… all….water…tar)	℃	Class 1 PAH	#
	Aerosol formation, clouding	mg/m³	Class 2 BTXE-S	#
	Deposition, condensation	mg/m³	Class 3 Pyrolysis (sub-)	#
	Gravimetric procedure Capture 100% Residue x%, share of…100%	mg/m³	Class 4 (Oxogenates, asphaltenes,..)	#
	Solids Temp. **independent** (Char,…) Temp. **dependent** (salts,…agglomerates,….)	mg/m³	Transient field: S-organics,… See chemical parameters	
	Freight, Deposition, intake, … Change of oil conditions (gas engine)	Mass/energy	S, N, Cl-Groups See chemical parameters	

 # a range of good bad, average to be defined

Quality = fulfilment of limits defined applications/consumers/treatment/gas producers

Gasengine without turbo charger & intercooler

Type of parameter	Physical defined limits Physically constituted		Chemically or of constitution clear defined	
	Dew point	#	Class 1	#
	Aerosol formation clouding	#	Class 2	#
	deposition	#	Class 3	#
	Gravimetric procedure Capture 100% Residue x%, share of…	#	Class 4	#
	Freight, Deposition, intake, … Change of oil conditions	#		
	Solids Temp. independent (Char,…) Temp. dependent (salts,…agglomerates,….)			

Multistage treatment for syngas

Type of parameter	Physical defined limits Physically constituted		Chemically or of constitution clear defined	
			ss 1	#
			ss 2	#
			ss 3	#
			ss 4	#

Application 1
Application 2
Application n

Fuel cell with hot supply & hot treatment

Type of parameter	Physical defined limits Physically constituted		Chemically or of constitution clear defined	
	Dew point	#	Class 1	#
	Aerosol formation clouding	#	Class 2	#
	deposition	#	Class 3	#
	Gravimetric procedure Capture 100% Residue x%, share of…	#	Class 4	#
	Freight, Deposition, intake, … Change of oil conditions	#		
	Solids Temp. independent (Char,…) Temp. dependent (salts,…agglomerates,….)			

Gasengine with turbo charger & intercooler

Type of parameter	Physical defined limits Physically constituted		Chemically or of constitution clear defined	
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	Gravimetric procedure Capture 100% Residue x%, share of…	#	Class 4	#
	Freight, Deposition, intake, … Change of oil conditions	#		
	Solids Temp. independent (Char,…) Temp. dependent (salts,…agglomerates,….)			

Codex:
Quality recommendations
for operation of…(consumers)

Comparability of diff. gasifiers…

Handling of method…(sampling, treatment,..)

Coupling of technologies…


H. Bosch 1450-1516

Webinars

Convent. Tar & particle

- agenda
  - #
  - #
  - #
  - #

Quantification of Water, Treatment of Sample Gas ‚Gasanalysis‘

- agenda
  - #
  - #
  - #
  - #

Sulphur-Organics

- agenda
  - #
  - #
  - #
  - #
- Inars started

Host-sites Round-Robin-tests

- agenda
  - Cross cutting
  - Host-site 1
  - Host-site 2
  - Host-site 3
- Inars started

Update CEN /TS

- agenda
  - Organisations (former actives)
  - Status in standardisation
  - **Learnings**
  - Targets of CEN
  - …….. Development of other TS

Testgas-generators

- agenda
  - #
  - #
  - #
  - #

Targets: gasification/pyrolysis/others (parallels S,..)
Key-person+substitute (long expertise)

Webinars: DETAILS Workshop: key items, ey catchers

Information (+Policy) Technology

Timetable Round Robin

Stage 1 (internal tests)

Flexible ending horizon

Tars
Water
Chem-Group [S, N,Cl]

Hosts presented

Status reporting

Stage 2 sample exchange

Tars
Water

Detail plan

Consensual advices

08/2013

Ending for official reporting requested

Stage 3 (hoste sites)

Tars
S-compounds
Water
Chem-Group [S, N,Cl]

Result reporting

CONFERENCE 2014

now **workshop** KO of St 2 KO of St 3 12/2013 03/2014

Time axis

Web inars in 3-5 main Topic fields frequently happening

Advanced Multistage RoundRobin
(time axis see other slide)

Stage 1: *inhouse, peer-group*

- Internal Test of each single player (voluntary)
- E.g.: 'method in house' with reference system compared

Scientific target

- CEN/TS 15439: *sugg. for improvement*
- Testgas generators (Methods, applicati

2013 03/2013-12/2013

Stage 2: *analytical testroutine*

- **Testsamples 1-3l** of each sample*)
- Each participant receives 10 ml/GC/HPLC or 100ml grav. CEN/TS,…

*) produced or delivered from testsites or participants

- Statistic result assessment
- Reporting in Webinars

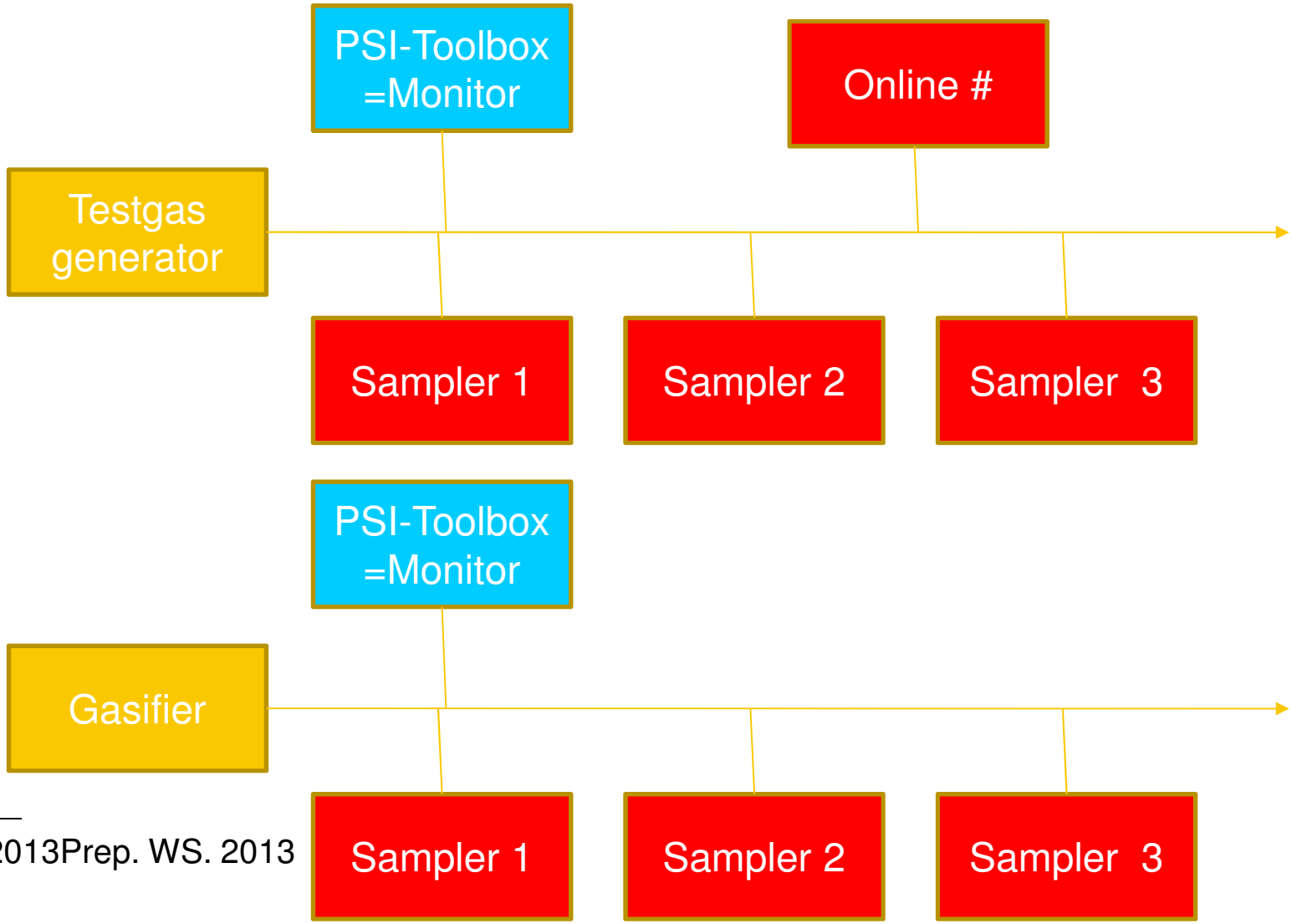
Stage 3: *live sample streaming*

- 3..4..xxx test sites/hosts (pre discussed on webinars 04-06/2013)
- Parallel sampling/measurements/ treatment/final analysis/reporting
- Degree of activity: Observing/samples (liquid/SPE)/active sampling

- Statistic result assessment
- Reporting webinars
- Optional **publication**

06/2013-03/2014

Round-robin Stage III



(Gas-)Quality = fulfilment of limits defined

Codex:
(Gas-)Quality recommendations
for operation of……. (consumers)

Comparability of diff. gasifiers…

Handling of method…

Coupling of technologies…

Selective ‘Charts of gas recommendations’ for Gas quality:
Responsible parameter (effects, discrete = compounds,…)

Sampling parameter, Conditions, Range

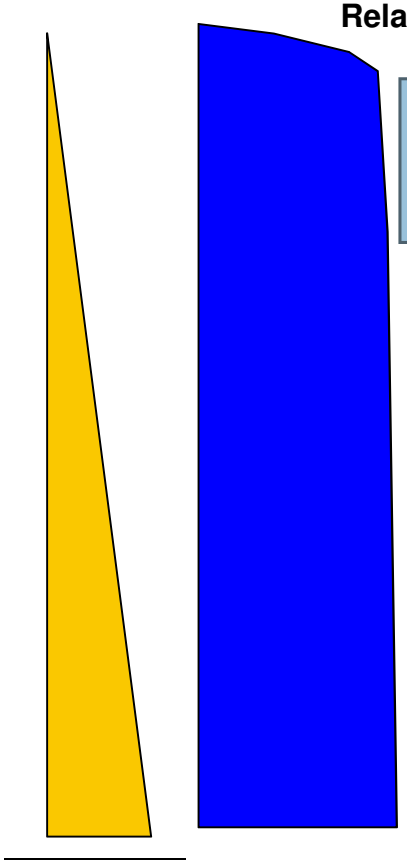
Relative Gas volume
V_{Gas}/V_{Liquid}

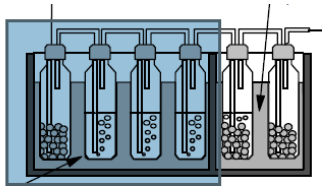
Relative capture

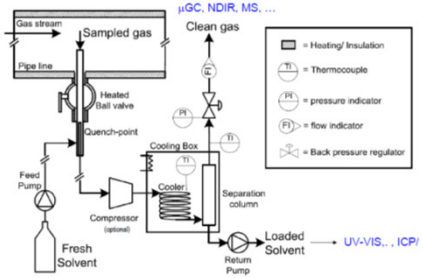
Sampling must
Deliver satisfactory
capture of compounds
looked for.

Analysis (=detection)
Must be sensitive
enough for
expected level.

Range of detection







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10- 0.1 mg/m³
'chromatographic procedures'

1-0.01 mg/m³
'trace procedures'

correctly

incorrectly

In General: Sampling must be **more complete** than the Analysis **can see.**

Parameter-stamp: e.g. *Gas engine with TC and IC*

Physical defined limits; Physically constituted		**Chemically; of constitution clear defined**	
Dew point (of… all….water…tar): *at 2 bar overpressure*	**Water: lower than 30 °C** **Tar: lower than 20 °C** **Calculated dew point <20 °C**	Class 1 PAH	**Napth. < 5mg/m³**
Aerosol formation, clouding *) *Optional at 2 bar overpressure*	**Technical free over 40 °C**	Class 2 BTXE-S	**Benzene** **<1.000 mg/m³**
Deposition, condensation	**Technical free over 40 °C**	Class 3 Pyrolysis (sub-)	**Phenoles** **<100 mg/m³**
Gravimetric procedure Capture -10 °C Evaporation 50 °C	**<10 mg/m³ at 50 °C evaporation**	Class 4 (Oxogenates, asphaltenes,..)	**#**
Solids Temp. **independent** (Char,…) Temp. **dependent** (~~salts,~~…agglomerates,….)	**<10 mg/m³**	Freight, Deposition, intake, … Change of oil conditions (gas engine)	**Mass/energy**

*) e.g. optical turbidity: see the turbidity number of diesel-exhaust-emission

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Treated synthesis gas

Flue gas

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High dust
High tar
High water
High temperature

Treated gas
Medium dust
Medium tar
Medium water
Medium temperature

Finished gas
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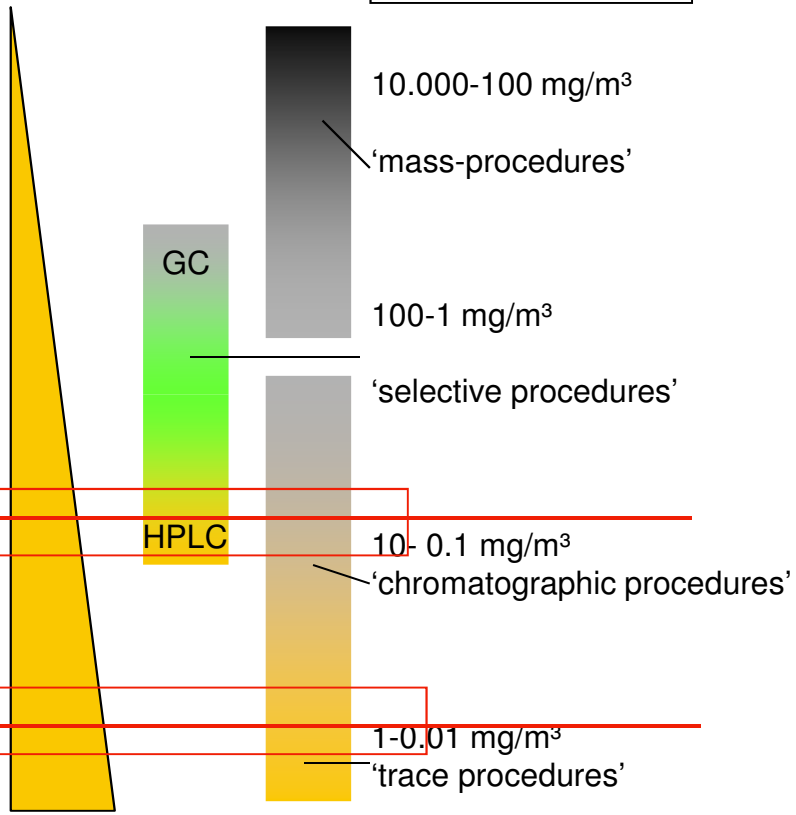
Low water
Ambient temperature



Sampling parameter, Conditions, Range

Particle ***Aerosol*** ***Tar***	Sampling conditions	Relative Gas volume V_{Gas}/V_{Liquid}	Range of detection

Particulate

Tar for grav.

Tar for HPLC

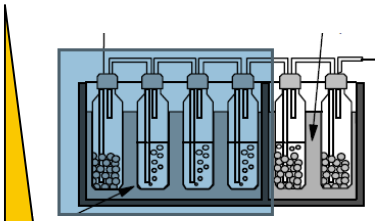
Tar for GC

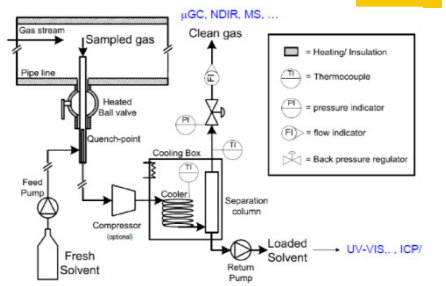
Tar similar comp.

Crude Gas
High dust
High tar
High water
High temperature

Treated gas
Medium dust
Medium tar
Medium water
Medium temperature

Finished gas
Low dust
Low tar
Low water
Ambient temperature





GC

HPLC

10.000-100 mg/m³
‘mass-procedures’

100-1 mg/m³
‘selective procedures’

10- 0.1 mg/m³
‘chromatographic procedures’

1-0.01 mg/m³
‘trace procedures’

In General: Sampling must be **more complete** than the Analysis **can see.**