bioenergy2020+

Method catalogue

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Bioenergy2020+

Graz, Austria

Content

- Model of former method catalogues
- Quality definitions
- Minimum requirements
- Qualification of each method

Benchmark: VTT method deskription

- 1st complete catalogue of different sampling and detections fundamentals *(vtt, 1998)*
- Most but not all analysis and quantification methods documented

VTT TIEDOTTEITA – MEDDELANDEN – RESEARCH NOTES 1903

VTT

TECHNICAL RESEARCH CENTRE OF FINLAND
ESPOO 1998

Sampling of contaminants from product gases of biomass gasifiers

Pekka Ståhlberg, Maija Lappi, Esa Kurkela, Pekka Simell, Pia Oesch & Matti Nieminen
VTT Energy

Definitions (1)

Quality= Fulfilment of defined targets in defined and repeatable measurable parameters.

About Detection and Quantification:

Nachweisgrenze / Detection limit / il limite di attestazione
LOD is the limit of detection from which the measured parameter is detected with a likelyhood of 50%.
The result is YES or NO.
Probable values below are called in-detectable or not to be detected with the present procedure/and/or detector.

Calculation from statistics: LOD= $\overline{X}$+n* σ

……..with mean $\overline{X}$ of blank value and IT's standard deviation of ±σ.

e.g. an analysis delivers the **detection**, if it exeeds 3-times the σ.

Definitions (2)

Erfassungsgrenze / Detection limit / il livello di registrazione
DL is the concentration level, from which the desidered substance is detected within an confidence range better than 95 or 99% (confidence intervall in normal distribution).

Calculation from statistics: DL~2*LOD

e.g. an analysis delivers the detection, if it exeeds 2-times the LOD.

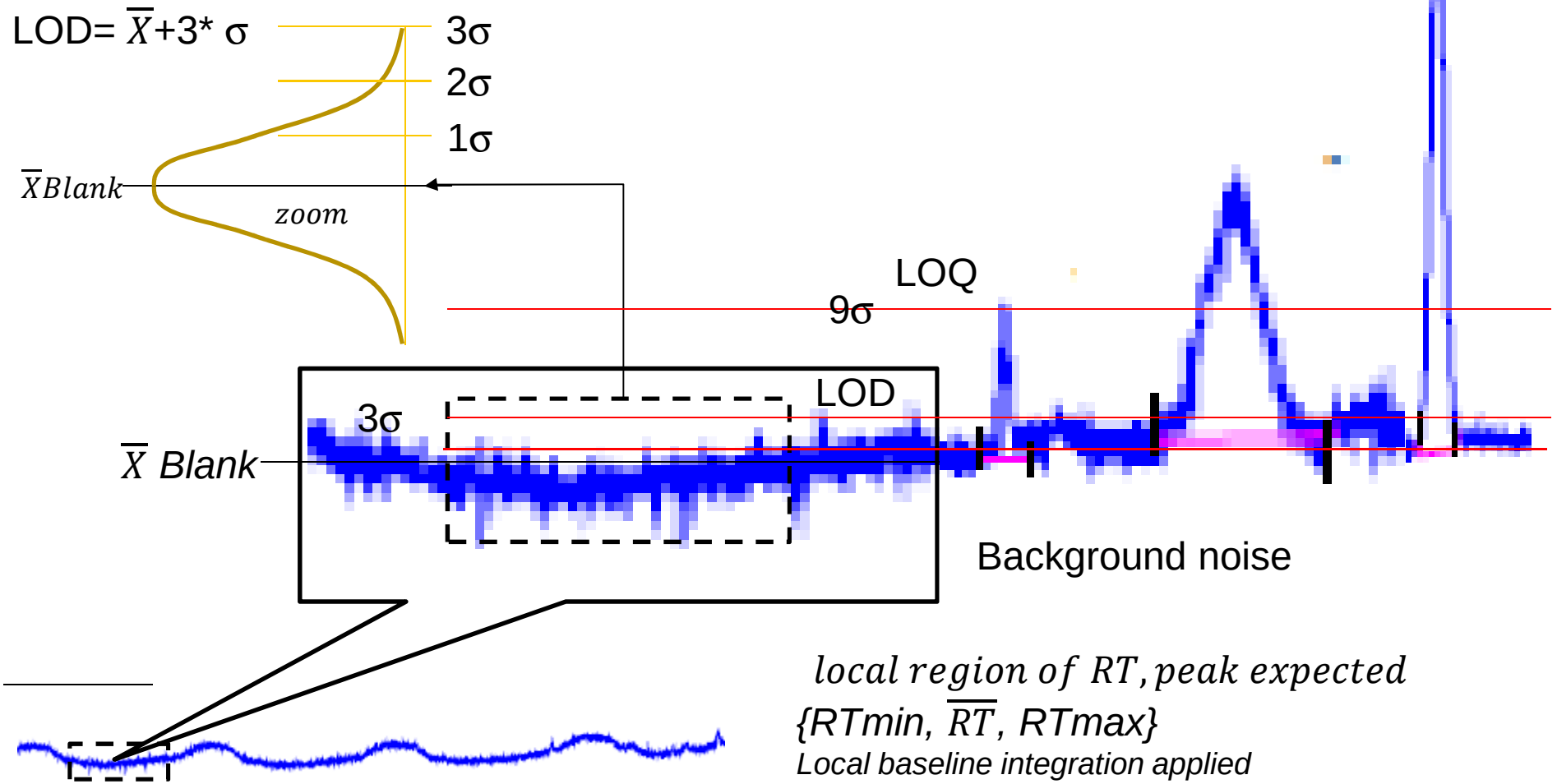
Bestimmungsgrenze / Limit of Quantification / il livello di quantificazione
Is the minimal limit from which a result can be reported with defined statistic information like RSD, or stat. deviation. The statistic computation is the same like LOD, but higher increment of sb:

LOQ= $\overline{X}$+n* σ ……..with mean of blank value ($\overline{X}$) and IT's standard deviation of $\pm\,\sigma$.
e.g. an analysis delivers the **quantification**, if it exeeds 9-times the $\pm\,\sigma$.

Or LOQ ~3*LOD

Definit
graphic visualisation

Signal shown: e.g. with peak height (for easier visualisation): real with ref.-peak an integration from different dilutions, sufficient linearity of the detector necessary.



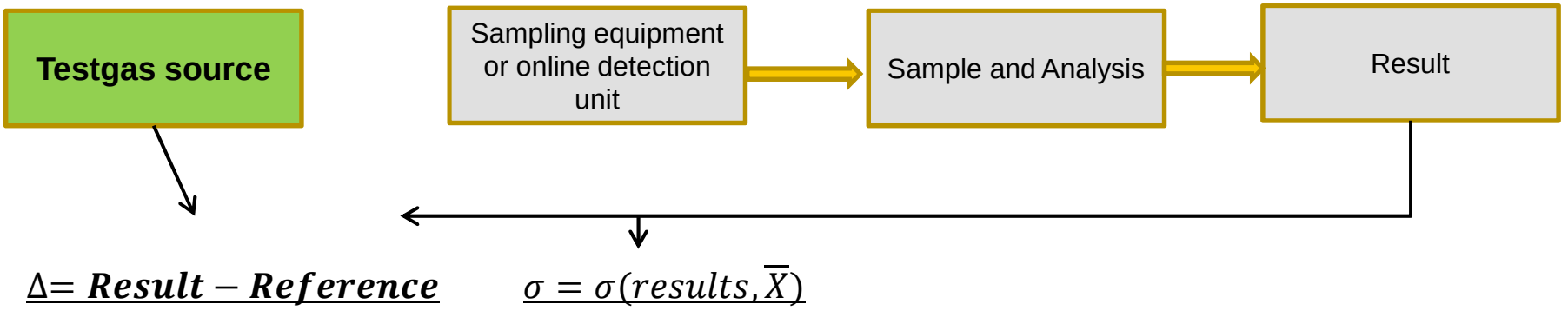
$local\ region\ of\ RT, peak\ expected$

{RTmin, $\overline{RT}$, RTmax}

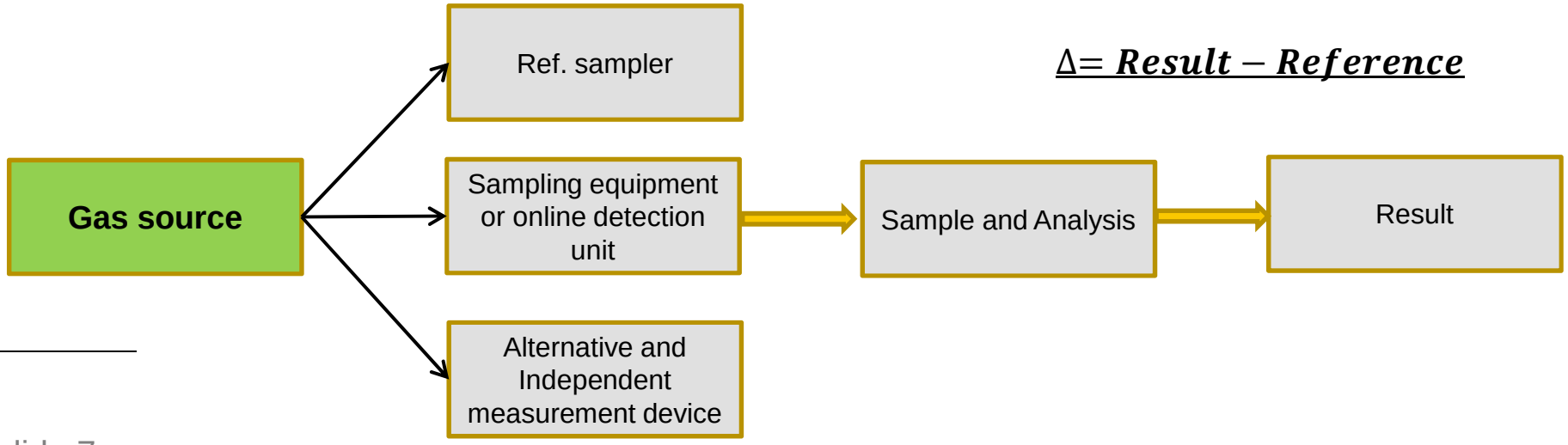
Local baseline integration applied

Quality measures
1. reference measurements for sampling

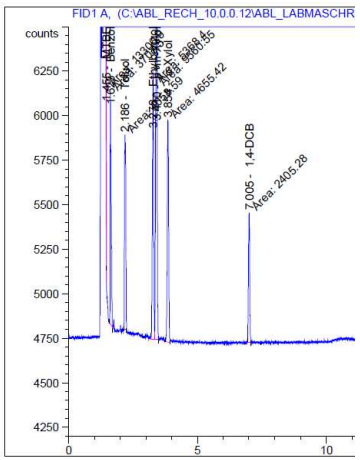
Test procedure 1: a reference gas (cylinder) or a test gas generator is available.

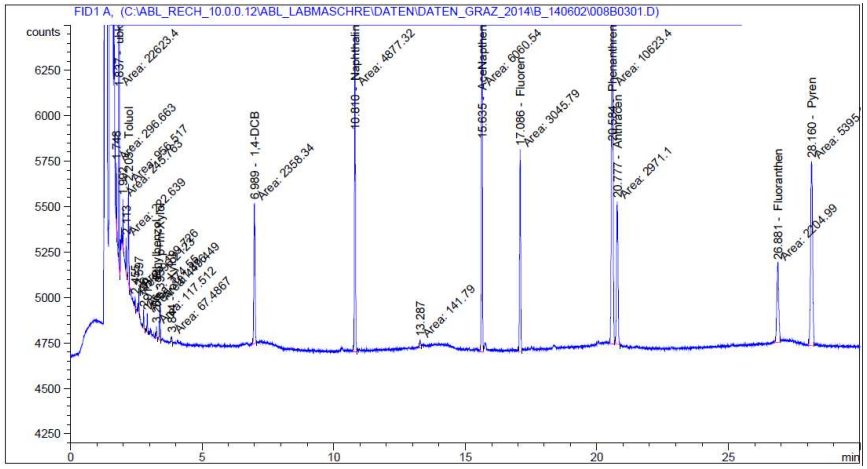


Test procedure 2: a reference sampler or / and an alternative device is synchronous available.



Quality measures
2. reprocessive quality control in Analysis (e.g.GC)





1.st run
For statistics in RT (identification).

2.nd run
Calibration of single compounds

3.rd check run
Test the analysis and repeatability.

4.th routine check run ‚control sample'
Test the daily performance.

Identification and RT-statistics (RT-Lock) and IST
If necessary adaptions of methods

Calibration data and RT-statistics
Check IST or ref. substance

Quality control report

Calibration data sheet & statistics Response & RT

Data

forward

Quantification sheet and control samples

Additional statistics

Data

forward

Sample result reporting

Quality measures
2. reprocessive quality control in Analysis (e.g.GC)

Zusammenfassung der Kalibrierdaten											Kalibration	
Name		Reihenfolge	PAK 4 ST	PAK 4-9 ST	EPA 525 mixA	EPA 525 sonst.	RT:	kurz	Streu RT	Streu RT	bis 10	RSD
							[min]		[min]	[%]	[mg/l*µl] pro count	[-]
Naphthalin	x	1	X				10,815	PAK1	0,007	0,064	0,0001120	0,999947
AceNaphtylen												
AceNapthen	x	2		X	X		15,325	PAK2	0,249	1,624	0,0001040	0,72807
Fluoren	x	3	X		X		17,089	PAK3	0,004	0,025	0,0001590	0,889884
Phenanthren	x	4	X	X	X		20,587	PAK4	0,009	0,044	0,0001100	0,910404
Anthracen	x	5	X		X		20,779	PAK5	0,006	0,029	0,0001630	0,956516
Fluoranthen	x	6		X			26,889	PAK6	0,018	0,066	0,0006200	0,994412
Pyren	x	7		X	X		28,170	PAK7	0,012	0,044	0,0001150	0,806553
Chrysen	x	8		X	X		36,758	PAK8	0,016	0,045	0,0001020	0,710639
Benz(a)anthracen	x	9		X	X		37,029	PAK9	0,016	0,044	0,0001410	0,940199
Benz(b)fluoranthe	x	10			X		44,509	PAK10	0,015	0,033	0,0001690	0,984626
Benz(k)fluoranthe	x	11			X		44,688	PAK11	0,015	0,033	0,0001670	0,986008
Benz(a)pyren	x	12			X		46,545	PAK12	0,014	0,031	0,0001680	0,972149
Indeno(1,2,3-cd)py	x	13			X		53,566	PAK13	0,017	0,031	0,0001670	0,978407
Dibenzo(a,h)anthr	x	14			X		53,925	PAK14	0,016	0,030	0,0001630	0,982735
Benzo(ghi)perylen	x	15			X		54,961	PAK15	0,022	0,041	0,0001620	0,986175

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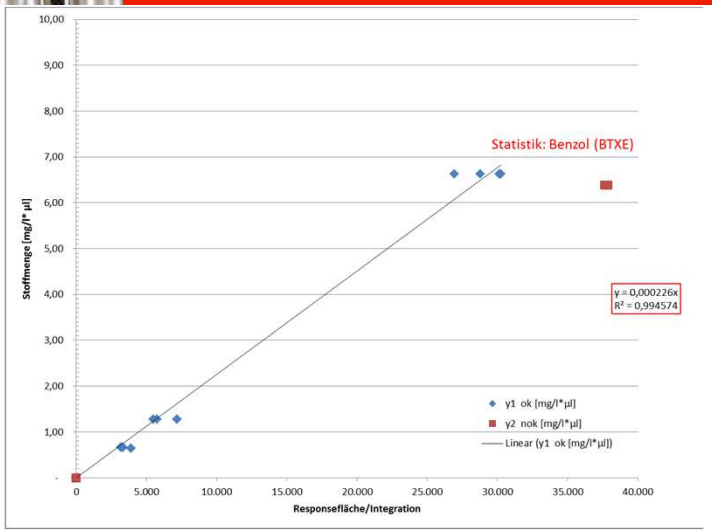
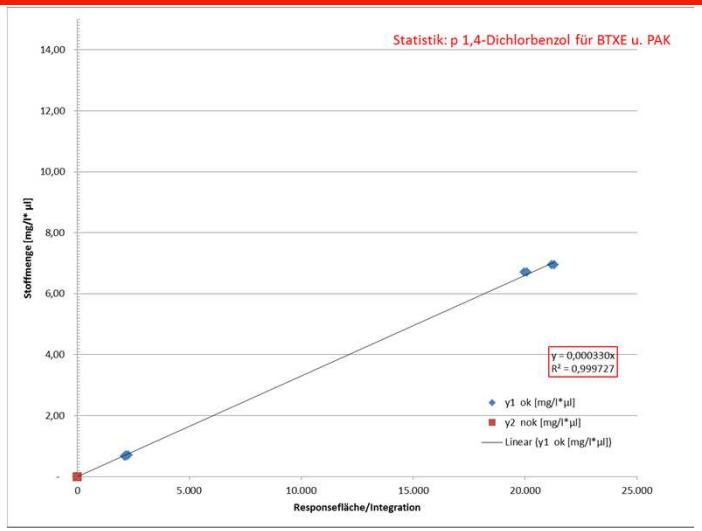
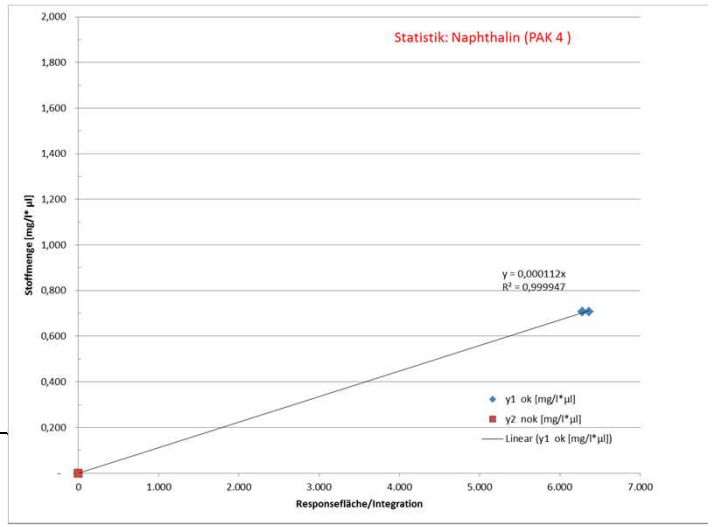
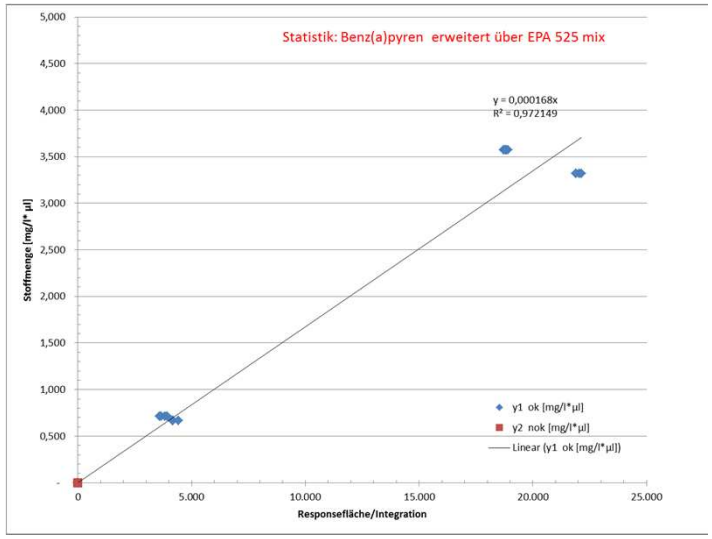








Application of toolboxes

	Offline sampling & later analysis		**online sampling & quasi cont. sampling**	**Real time sample extraction and/or detection/quantification**
	Accumulation on solid phase	Accumulation in liquids (cooled)	Dosage, fractioning chromatographic separation in retention	Dosage or dilution, selective detection & quantification
Necessary accessories	Dilution against water condensation	Pre-separation of solids/aerosols ‘dust-extraction’	Diff. pre-separations of solids/aerosols ‘dust-extraction’ & dehumidification	additional Measures against scaling, layering, deposition Online calibration
Benefit	Simple equipment Sample storable & transport	Sample storable & transport (heavy eqipment)	Quasi continous result reporting	All in real time
COSTS	**Very low**	**medium**	**high**	**Very high**

Method catalogue

(I cadastre; II catalogue; III evaluation checklist)

1. Method description
- Including the sampling
- Equipment
- Procedure
- Not to do's, safety measures

2. **Method is recommended** for the following
- Gas families*)
- Tar species
- Concentration range

*) matrices and accompanied impurities

3. **Method validation**
- On application
- Gas family
- Procedure
- Reference-method used,…..
- State of the art ref. methods in industry, petro chemistry,…
- Statistic results from RR-class 2 and 3

4. **Method development** or **rejection**

Targets of (2)+(3) evaluated:
- Which is recommended or not
- Which is old and now implemented in newer techniques

RR-class 2: based on sample exchange, RR-class 3: based on synchronous sampling, accompanied analysis.

Targets for measurements in gases

Status & degree of plant evolution	**Lab test for effect experiments**	**Lab plant with real feedstock**	**Pilot plant**	**Full commercial plant**
Purpose	Study in lab (e.g. reforming reaction)	Plant operation a. component testing	Plant operation a. plant testing & optimisation	Plant operation & further optimisation trouble shouting OR **authorities**
Substances #	1 and simple	1-3, Matrix defined	1-5, Matrix defined	3 most important, Matrix defined
Matrix				
Frequency of measurement	1/ minute, or online	1/ hour, or online	1/ hour, or 1/ shift	1/ hour, 1/ shift, 1/month 1/year
Type of result	Manny points, continuous curve	Manny points, continuous curve	Sufficient stable points, average/shift	Result protocol Plant control
Labour expectations	Expert from lab. familiar with all equipment	Expert from lab. available	External expert contacted	a) automated: continuously b) Periodically from external experts
Expert knowledge	Practical expert knowledge	Practical expert knowledge recommended	Practical expert knowledge recommended	Expert from service & maintenance, calibration, quality control.
Automation	Sample switching Control, Diff. software applications	Sample switching Control, Diff. software applications	Sample switching Control, via full plant control or	Automated = online Quality procedures

Degree of difficulties; scale

Temperature at sampling point	*Content of DUST*	*Content of WATER*	*Content of organics ('tars')*	*Compounds organic*	*Compounds in-organic*	*total*
1,000 → 4	>10,000 → 5	>80°C → 5	>10,000 → 5	**Manual**: Multiply x 1	**Manual**: Multiply x 1	
800 → 4	<10,000 → 5	<80°C → 3	<10,000 → 3			
600 → 4	<1000 → 3	<60 → 2	<1,000 → 2			
400 → 3	<100 → 2	<40 → 1	<100 → 1	**online**: Multiply x 10	**online**: Multiply x 5	
200 → 2	<10 → 1	<10	<10			
ambient	<1	<0°C	<1			
°C	mg/m³	dewpoint local pressure	mg/m³ dewing			

TF	+	DF	+	WF	+	OF	=		DEGREE
2+		2+		1+		2	=	normal application	7 (=medium)
4+		5+		3+		2	=	e.g. high dust fluidised bed sampling	14 high

Sampling of Benzene becomes more important

Typical raw gas: 500-10.000 mg Benzene/m³
Typical cleangas for gas engines (±turbo charger): 250-5.000 mg/m³

Residual concentrations in flue gas: 2-10% slip stream from product-fuel-gas
1-20% residues from break down of higher polyaromatics, additional from decomposed/burned lubricant.

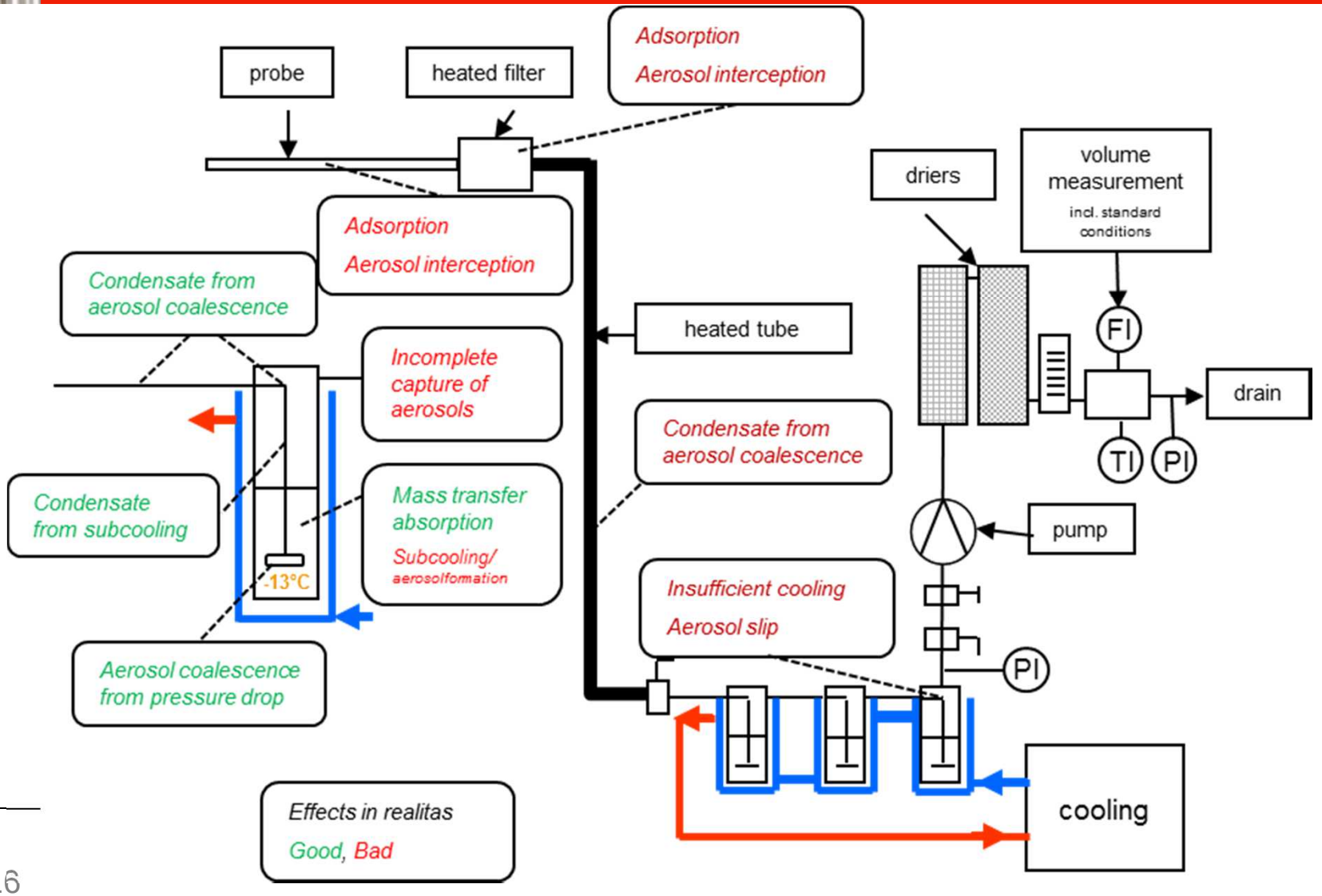
Concentrations to be detected: 1-10 mg/m³

Sampling stream is hot, contains oxygen and is very humid.

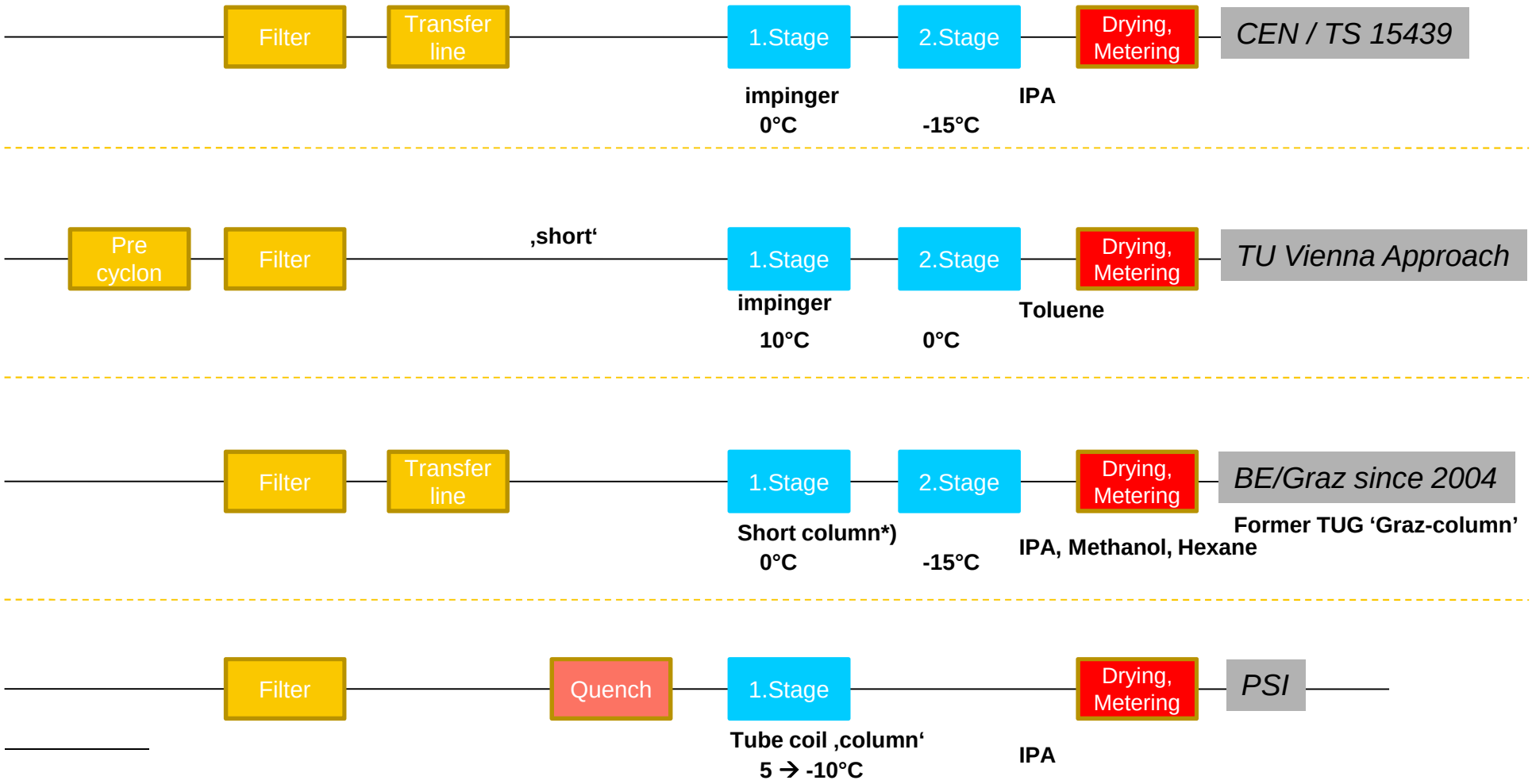
Further regulation via *TA-Luft* is expected (<5 mg/m³) beside limits of organic matter (<10 or 50 mg/m³).

Currently formaldehyde FA is not regulated, compared to NG-gas engines.

Effects all over the sampling line



Suitable Concepts ‘derivatives of CEN / TS 15439



Sampling parameter, Conditions, Range

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

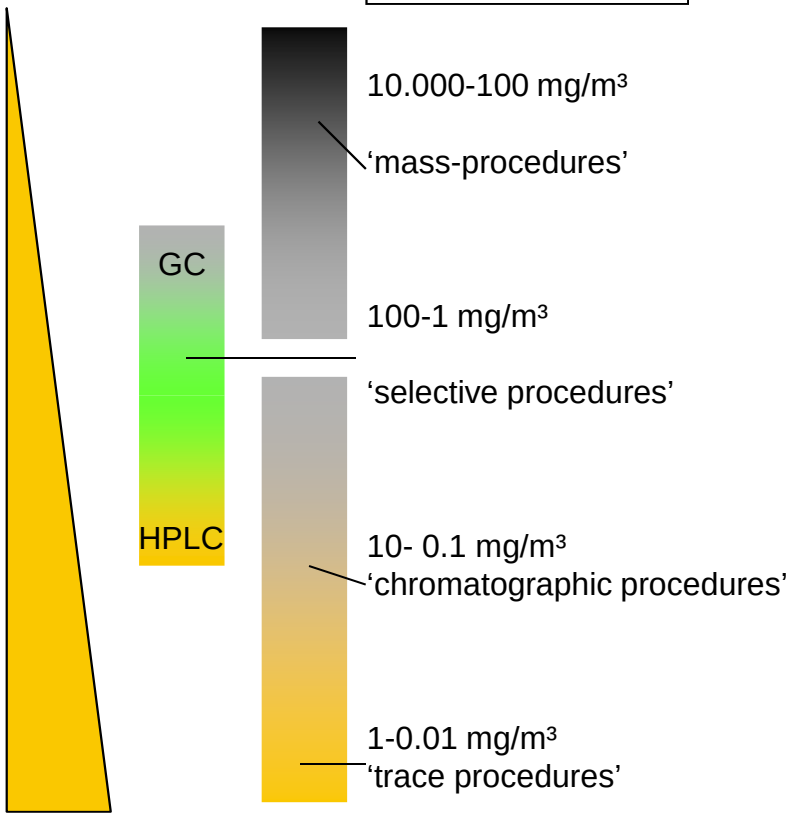
Particulate
Tar for grav.
Tar for HPLC
Tar for GC
Tar similar comp.

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

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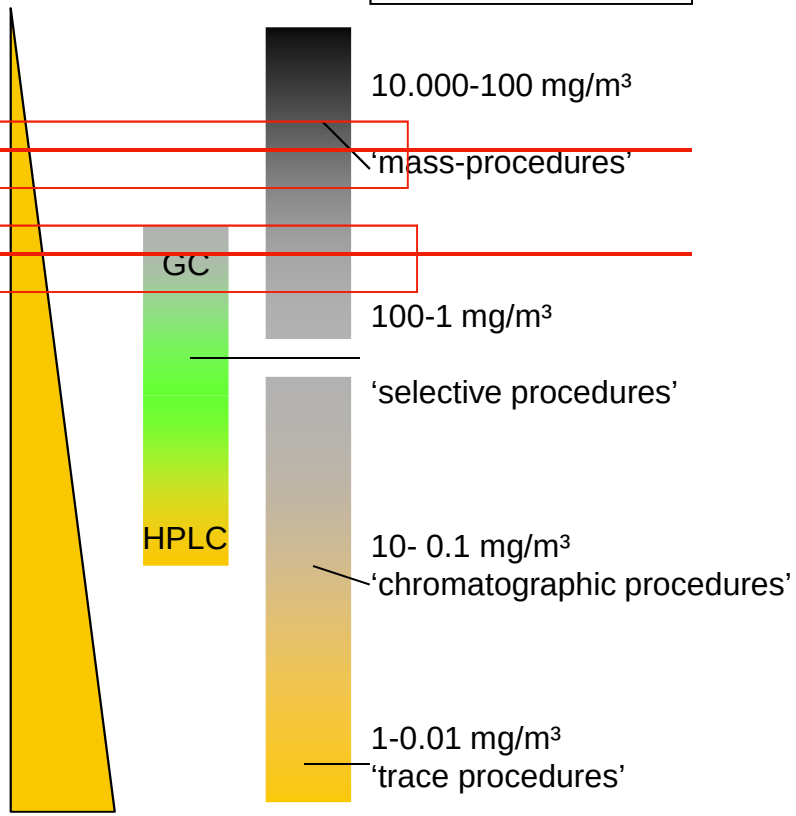
Finished gas
Low dust
Low tar
Low water
Ambient temperature
Very high pressure



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

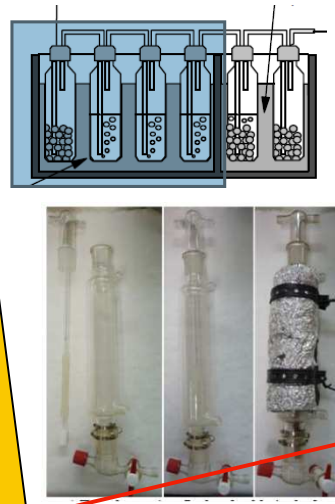
Relative Gas volume
V_{Gas}/V_{Liquid}

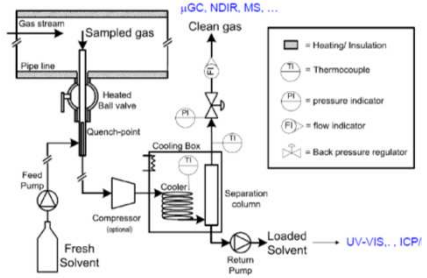
Relative capture

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





GC

HPLC

correctly

incorrectly

Range of detection

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.**