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Test gas generators; principles & fundamentals

Notes, Markus Kleinhappl, Stefan Martini

Bioenergy2020+

Graz, Austria

Content

- Quality measures
- Definitions
- Measurements=comparison, compare what with what?
- Workflow for typical calibration
- Fundamental basics
- Different systems

‘good to know, what You are expecting (measurements)’ *R. Slimane, 2014*

‘it’s difficult to make forecasts, especially, when they should be for the future’ K. Valentin; 1925

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

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 likely hood 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.

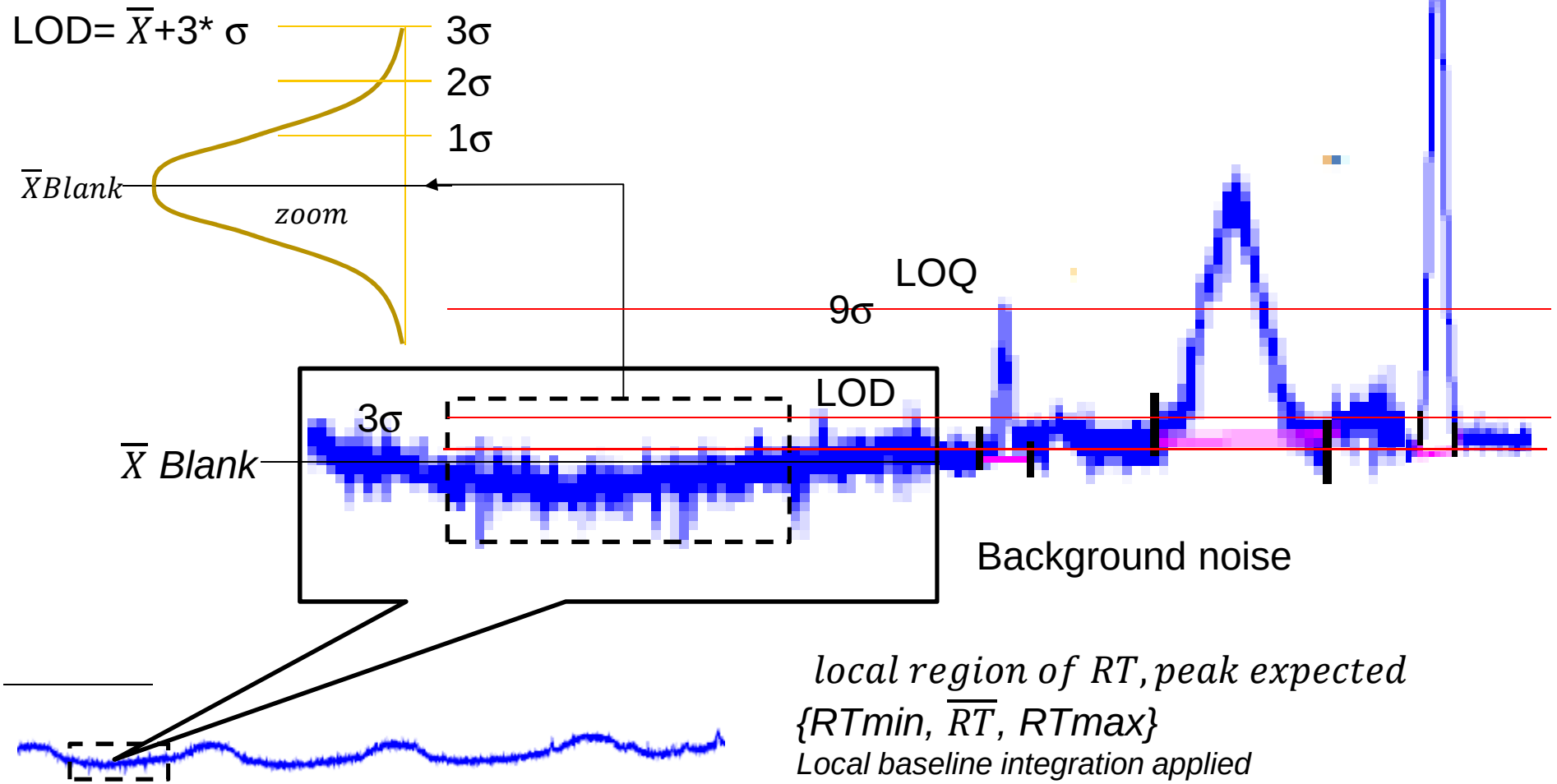
Bestimmungsgrenze / Limit of Quantification / il livello di quantificazione
Is the minimal limit from which a result can be reported with defined statistic information like RSD, or stat. deviation. The statistic computation is the same like LOD, but higher increment of sb:

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.



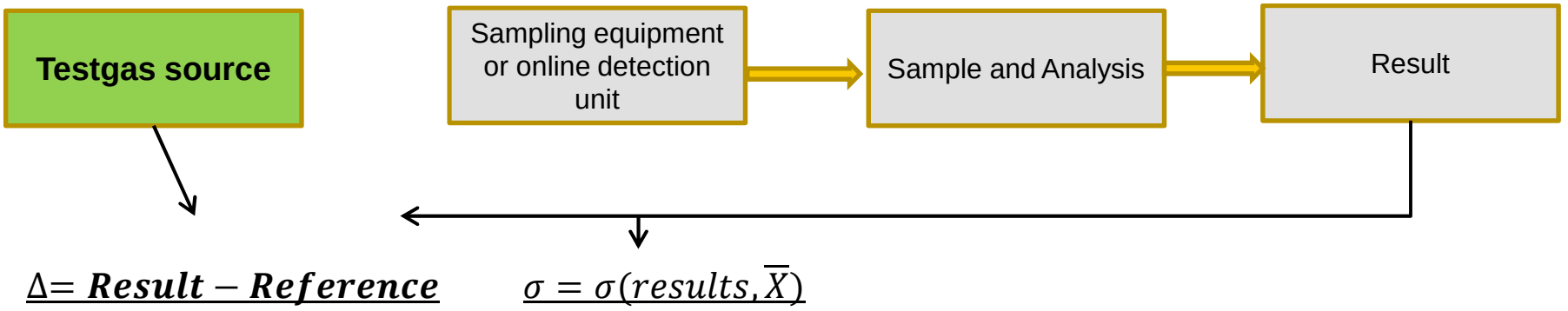
$local\ region\ of\ RT, peak\ expected$

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

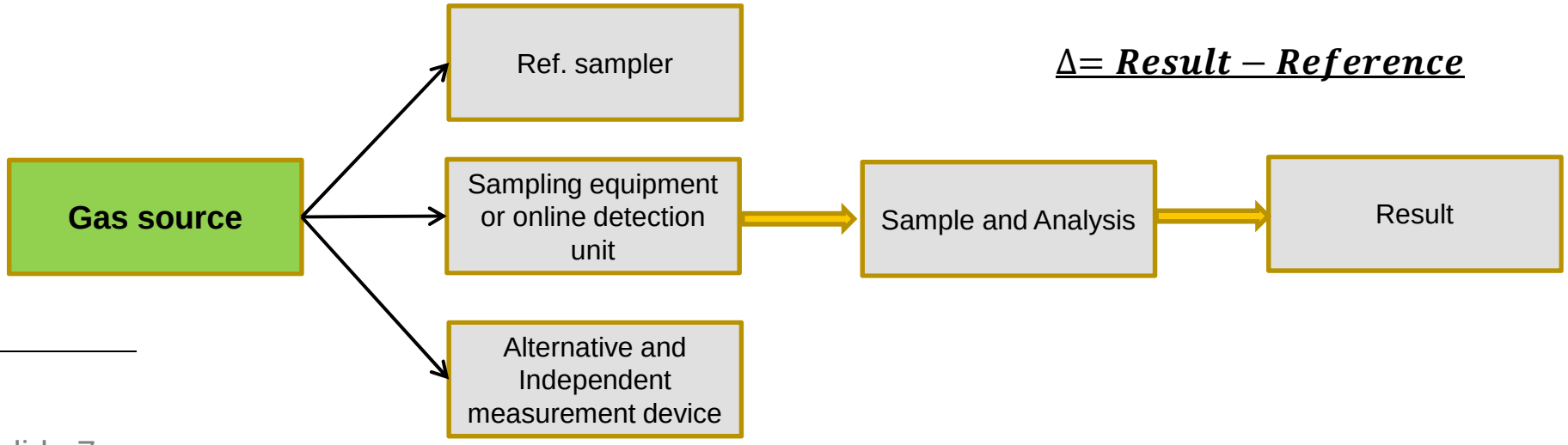
Local baseline integration applied

Quality measures
1. reference measurements for sampling

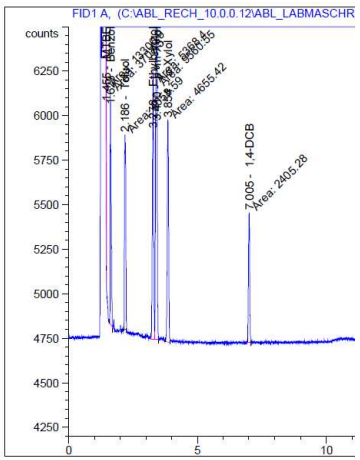
Test procedure 1: a reference gas (cylinder) or a test gas generator is available.

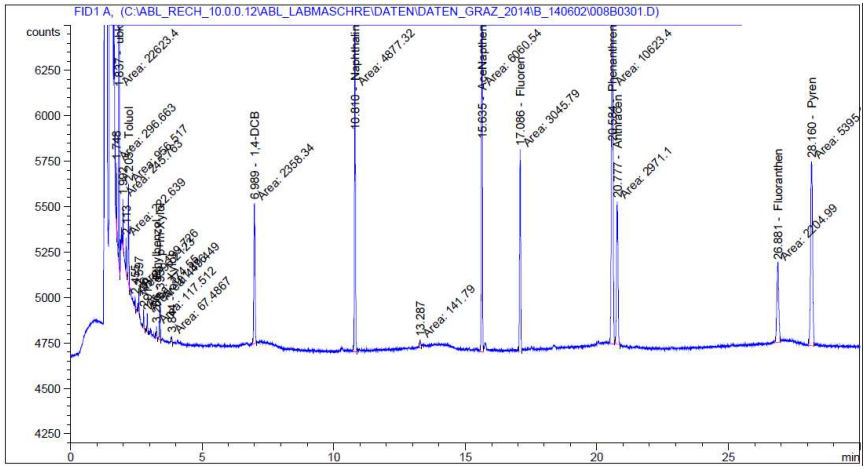


Test procedure 2: a reference sampler or / and an alternative device is synchronous available.



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

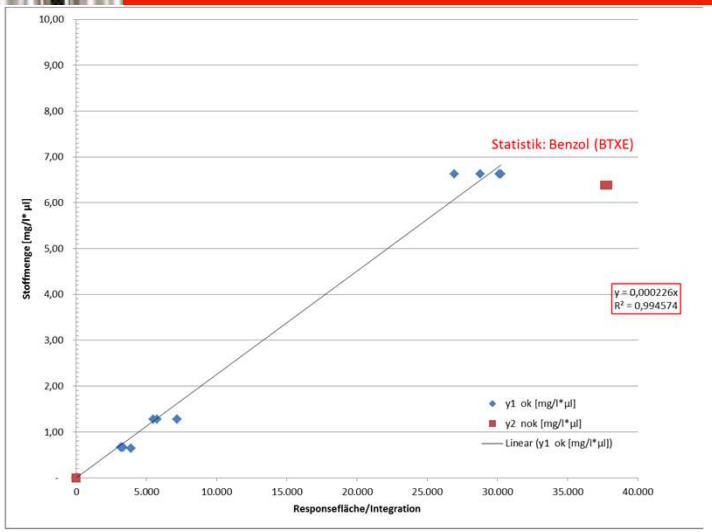
Additional statistics

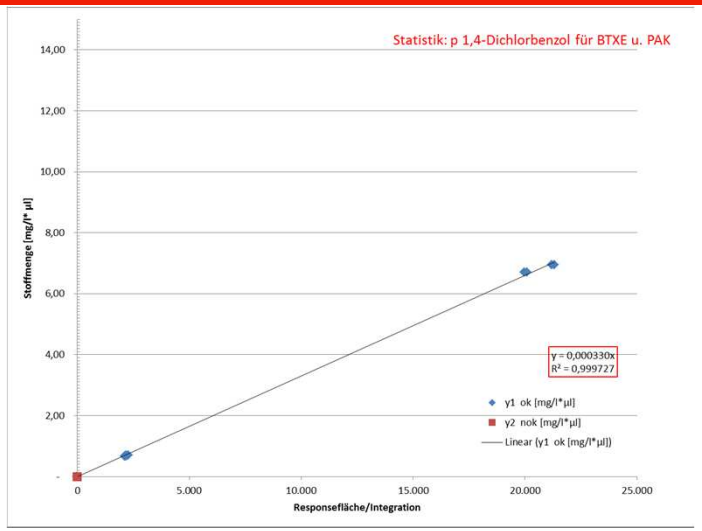
Data

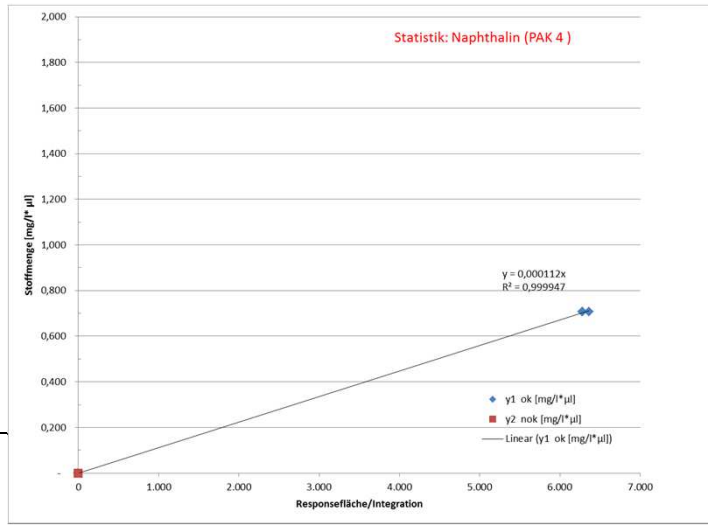
forward

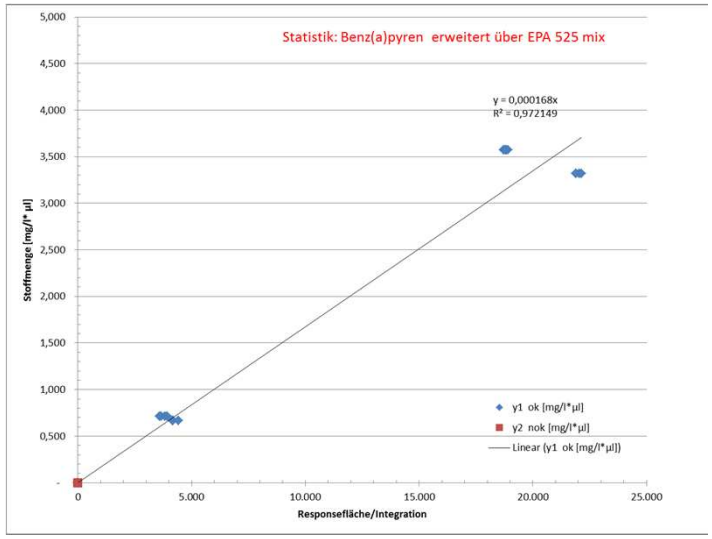
Sample result reporting

Quality measures
2. reprocessive quality control in Analysis

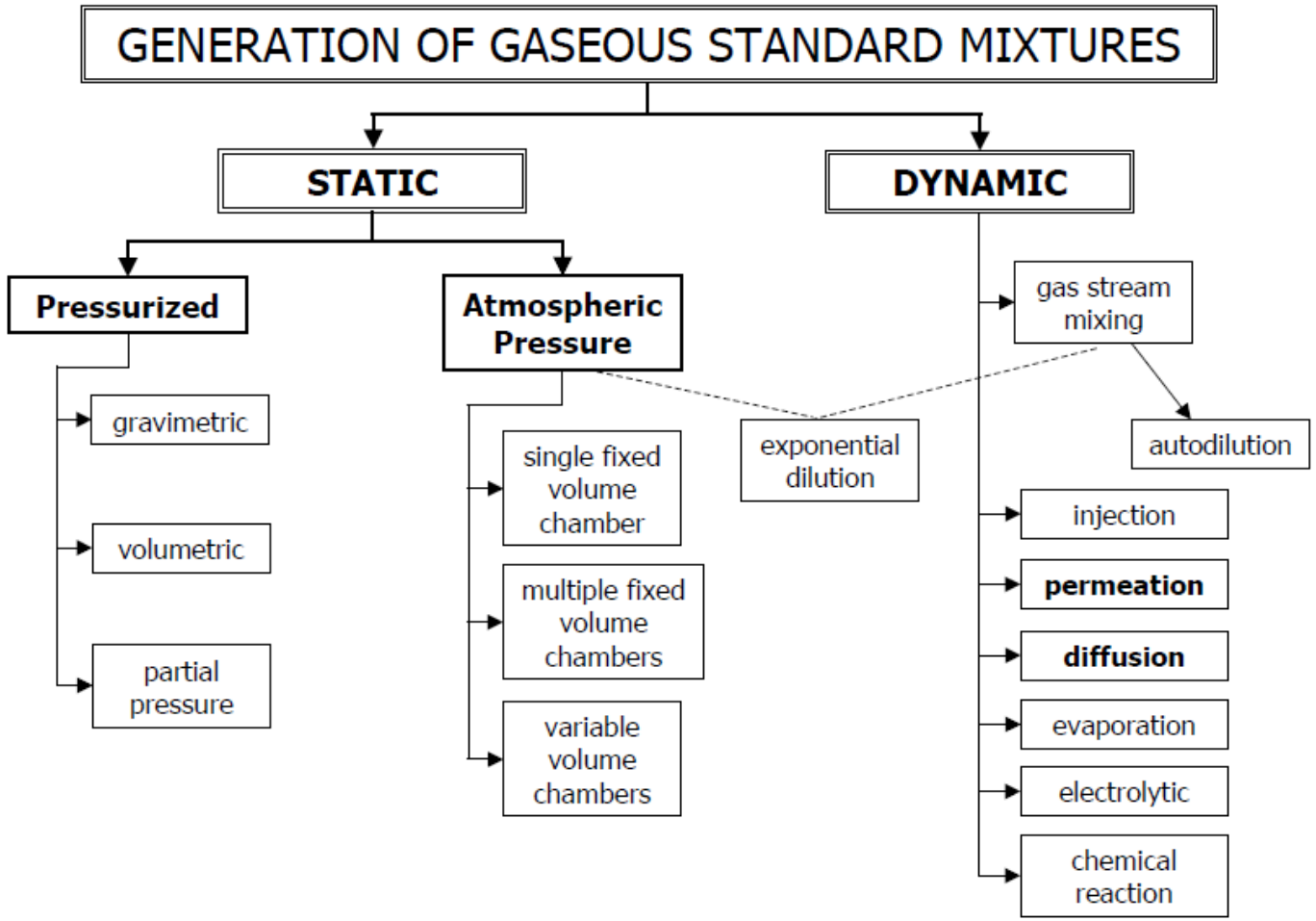








First systematics : How to do ‘test gas generators’; *Namiesnik 1984, …*



The general principles of 'test gas generators'

Dosage on mass or fixed volume

Dosage in **stationary gas volume** (fan or diffusion mixing). **Closed volume**

Dosage of **liquid flow into flow** of carrier gas (e.g. syringe and static mixers)

Other approaches like electro-chemical generation

C=c*Vol/Vol
C=c*mass/Vol

C=c*FlowVol/FlowVol
C=c*massFlow/FlowVol

Fundamental: BALANCE

Mixing flows & dilution

Mixing of precise metered flows, also from cylinders

C=c*FlowVol/(FlowVol+Diluter)
C=c*massFlow/(FlowVol+Diluter)

Fundamental: BALANCE

Dosage via thermodynamic-saturation/mass transfer

Mass flow with limited mass transfer= diffusion tubes or membranes

Saturation up to saturation-limits because of intensive mass transfer:

Sublimation (solid→ gas)

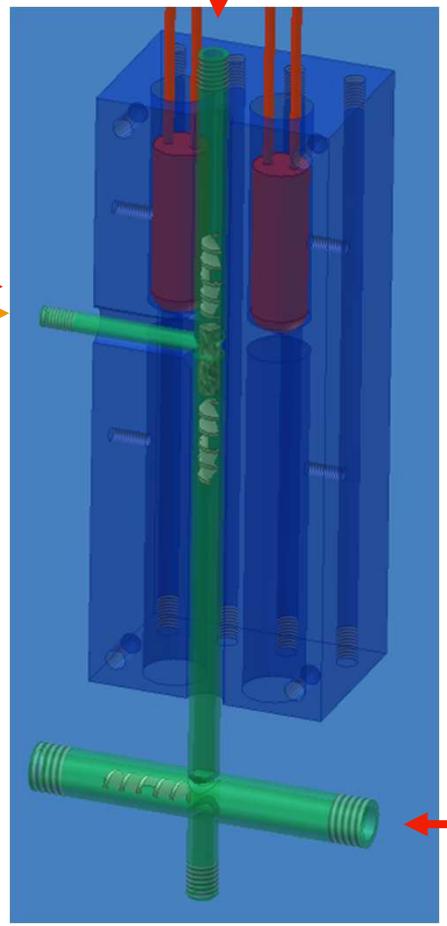
Evaporation (liquid → gas)

Fundamental: MASSTRANSFER and equilibriums

Fundamentals of dosage (enforced) generating

carrier

Solvent solution
of substance(s)



Evaporator for solvent

Heated alumina bloc with inserted evaporation-tube (compare GC-Injector). Following static mixing elements (swirl-anti-swirl)

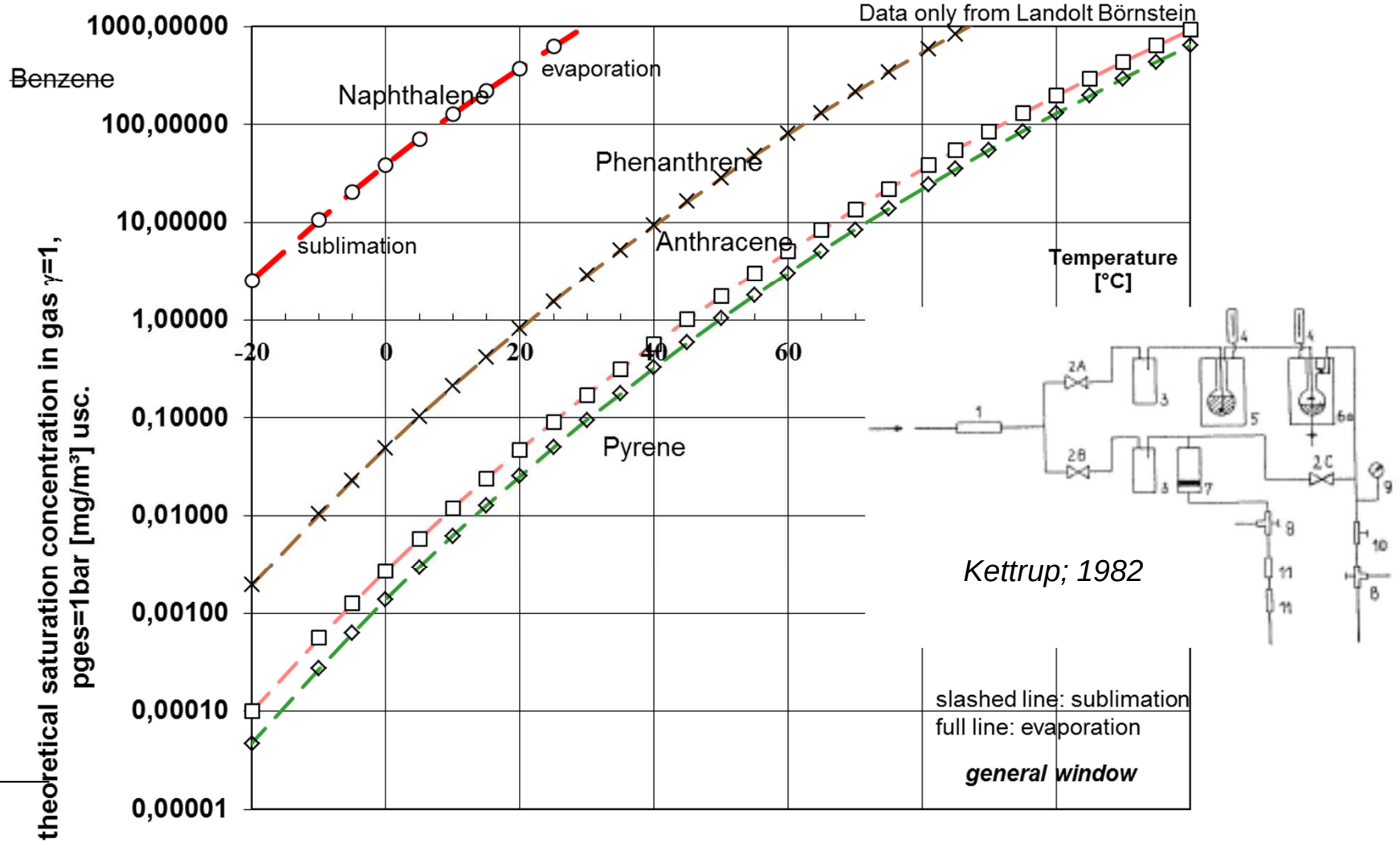
Materials: glass and PTFE

Stainless steel

Alternative with packing like a GC – liner (gooseneck).

Dilution: all other gases

Fundamentals of thermodynamic generating



Fundamentals of thermodynamic generating

Phase change thermodynamic of **pure** substances:

Vapour← → Liquid: evaporation and condensation

‚activity gas= activity liquid‘

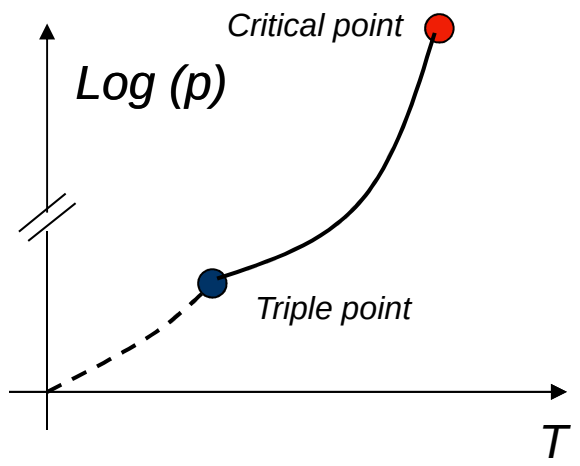
$$p_i = p_{total} \cdot y_i \cdot \varphi_i\Big|_{gas} = p_i^* \cdot x_i \cdot \gamma_i\Big|_{liquid}$$

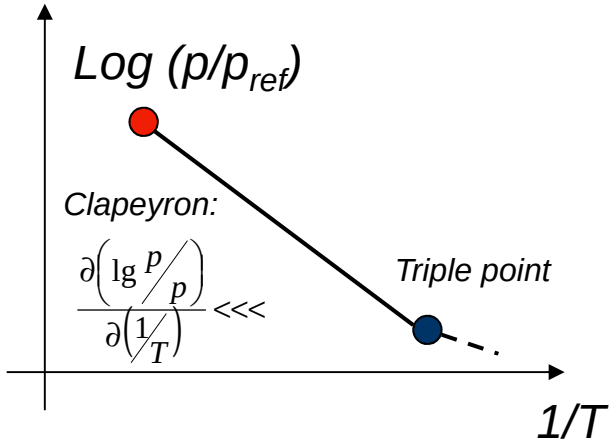
Vapour ← → Solid: sublimation and re-sublimation
‚activity gas = activity solid‘

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

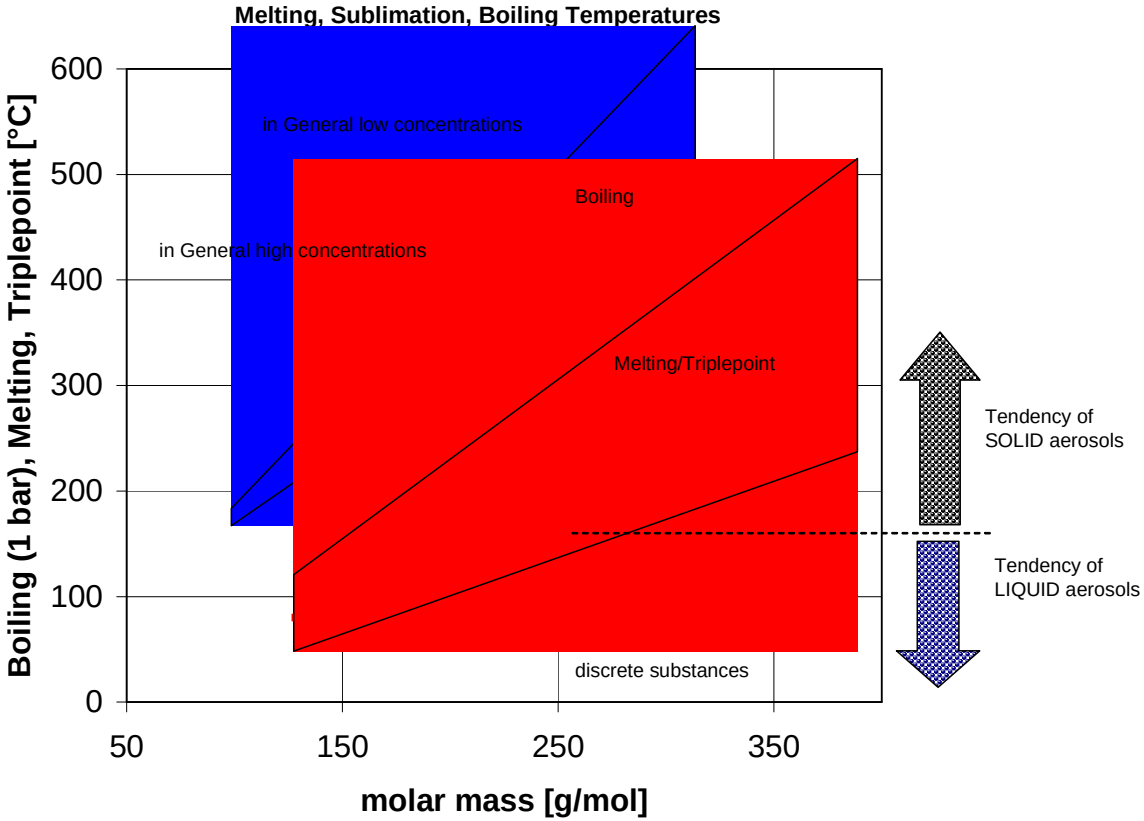
The clear and correct description of real substances
is not as easy as it looks.
(serveral data ref.; missing data,..)

known in general





Fundamentals of thermodynamic generating (PAH-data)



e.g. selection of PAH

		molar mass	boiling point	melting point
		[g/mol]	[°C]	[°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

Barbara system for test gases in cell- based toxicology: Purpose

General purpose:

Generating a testgas for ‘gasing’ on cell cultures for viability and toxicology tests.

Final targets:

Air/CO2- mixture as GAS (like breathing gas)

Humidity for saturation at 37°C (wet cell substrate)

Test components:

Terpenes

Aldehydes

Fully automated for operation around the clock.

General test application:

Terpenes: 0.1 to 100 mg/m³ (0°C and 1 atm)

Formaldehyde: 0.05 to 5 mg/m³ (0°C and 1 atm)

Further application for sampling calibration and validation, e.g. GC-sampling-valve validations & calibration

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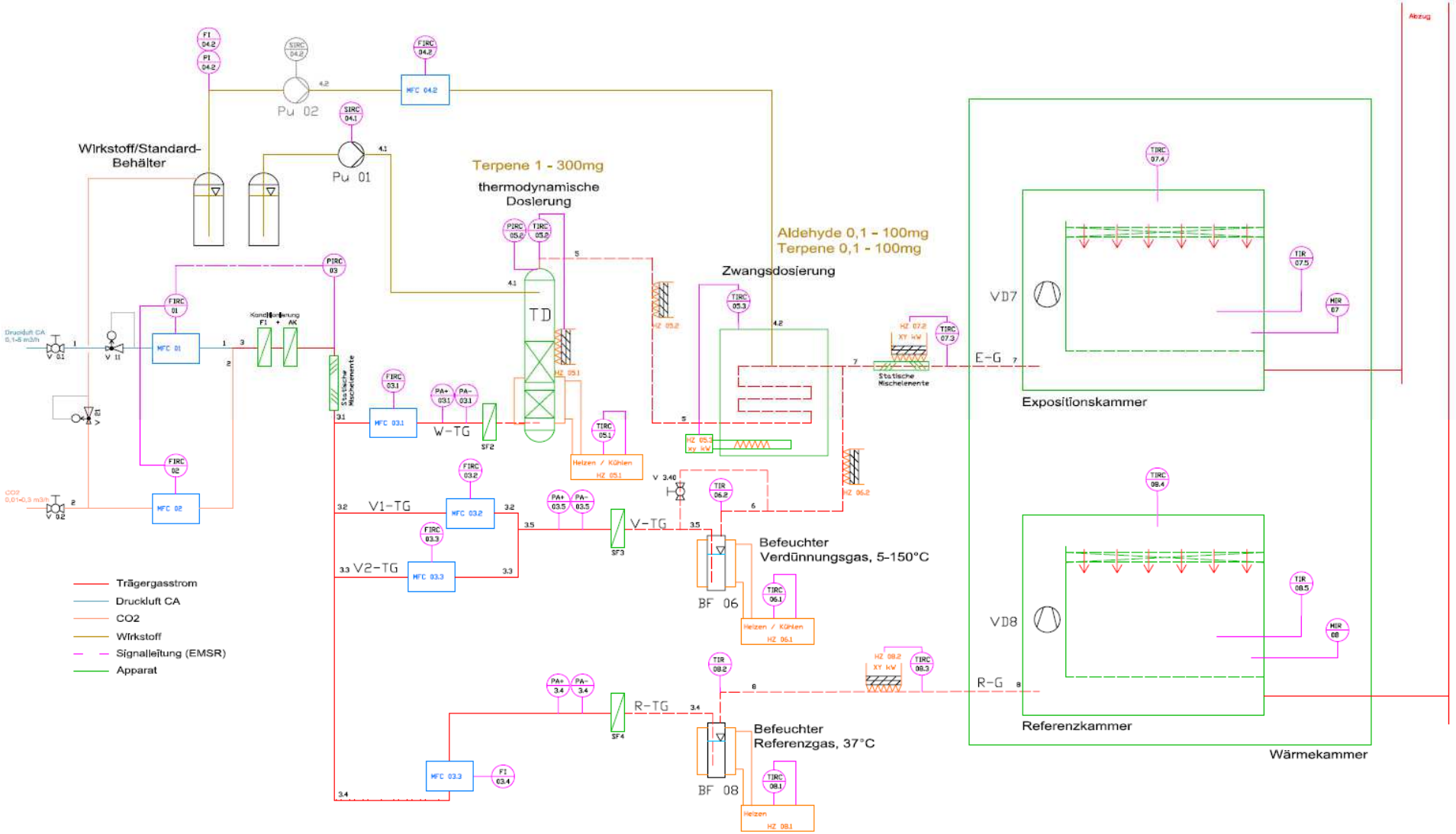
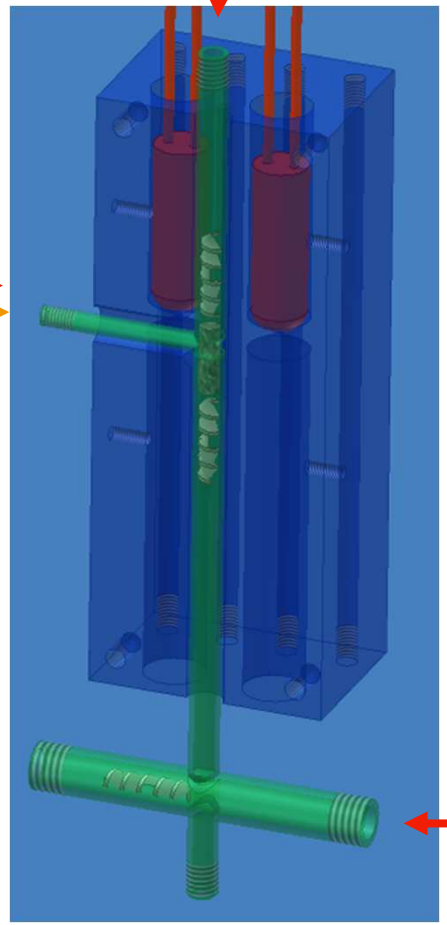
Barbara system for test gases in cell- based toxicology: total instrumentation



Barbara system for test gases in cell- based toxicology: enforced dosage of solvent

Air/CO_2

Solvent solution
of substance(s)



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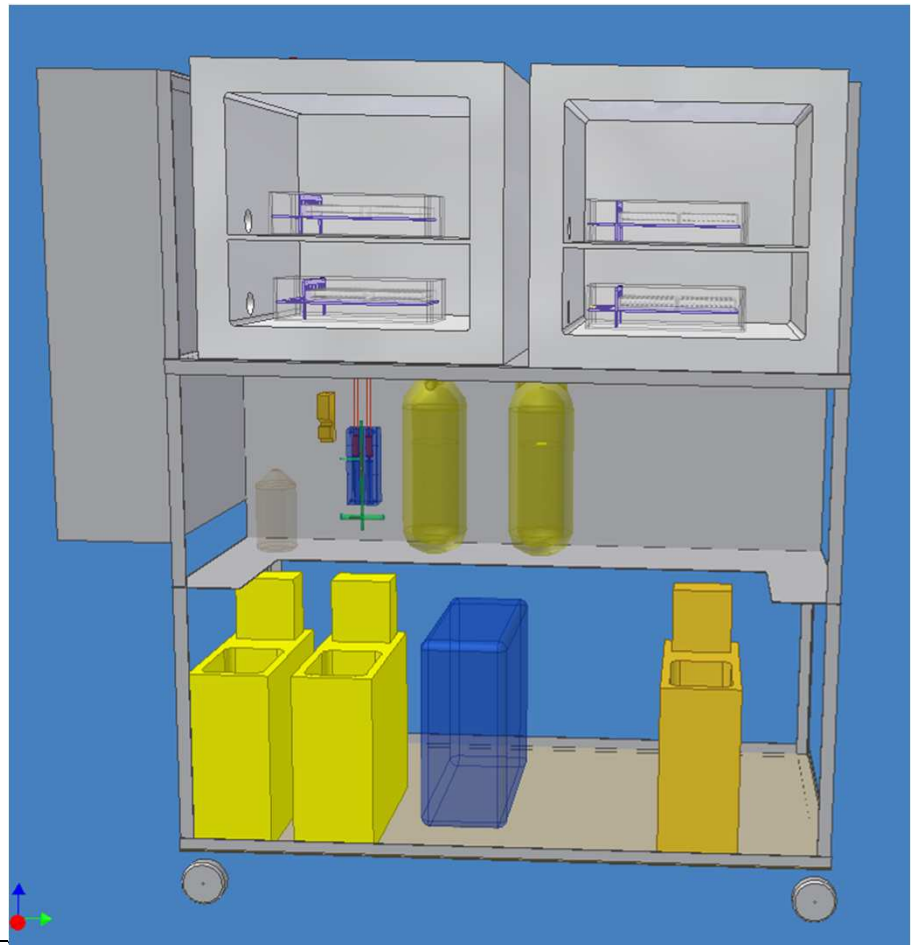
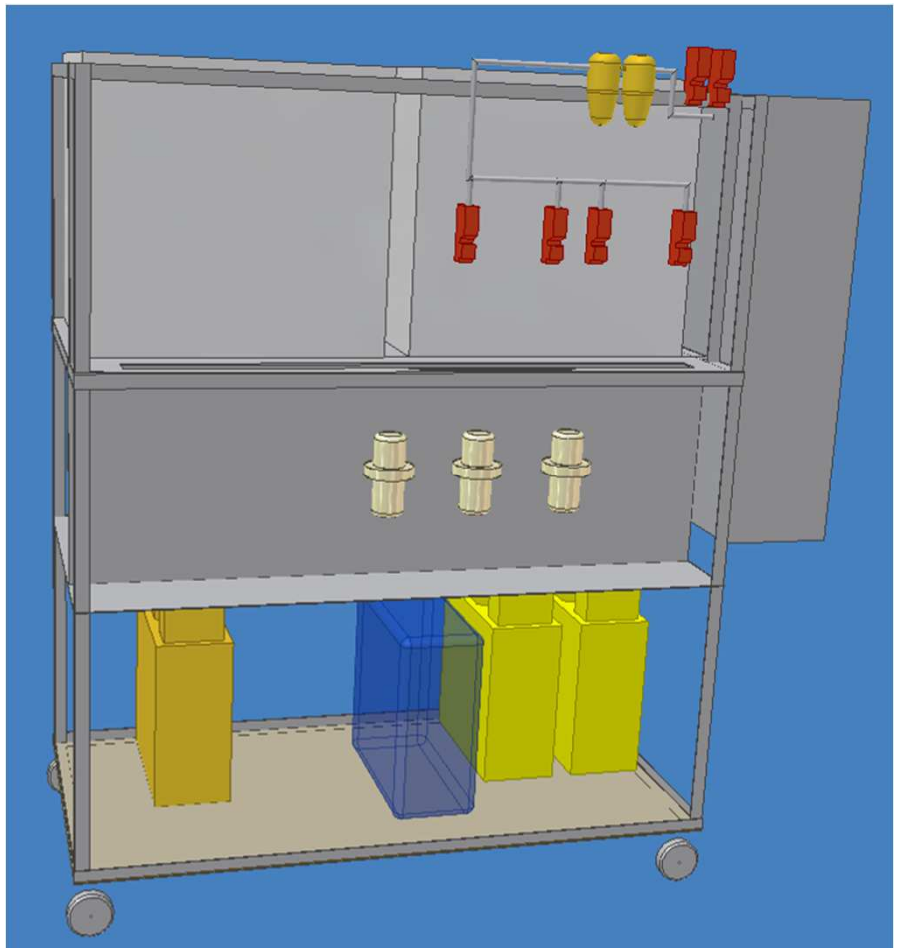
Barbara system for test gases in cell- based toxicology: conception





Barbara system for test gases in cell- based toxicology: reality

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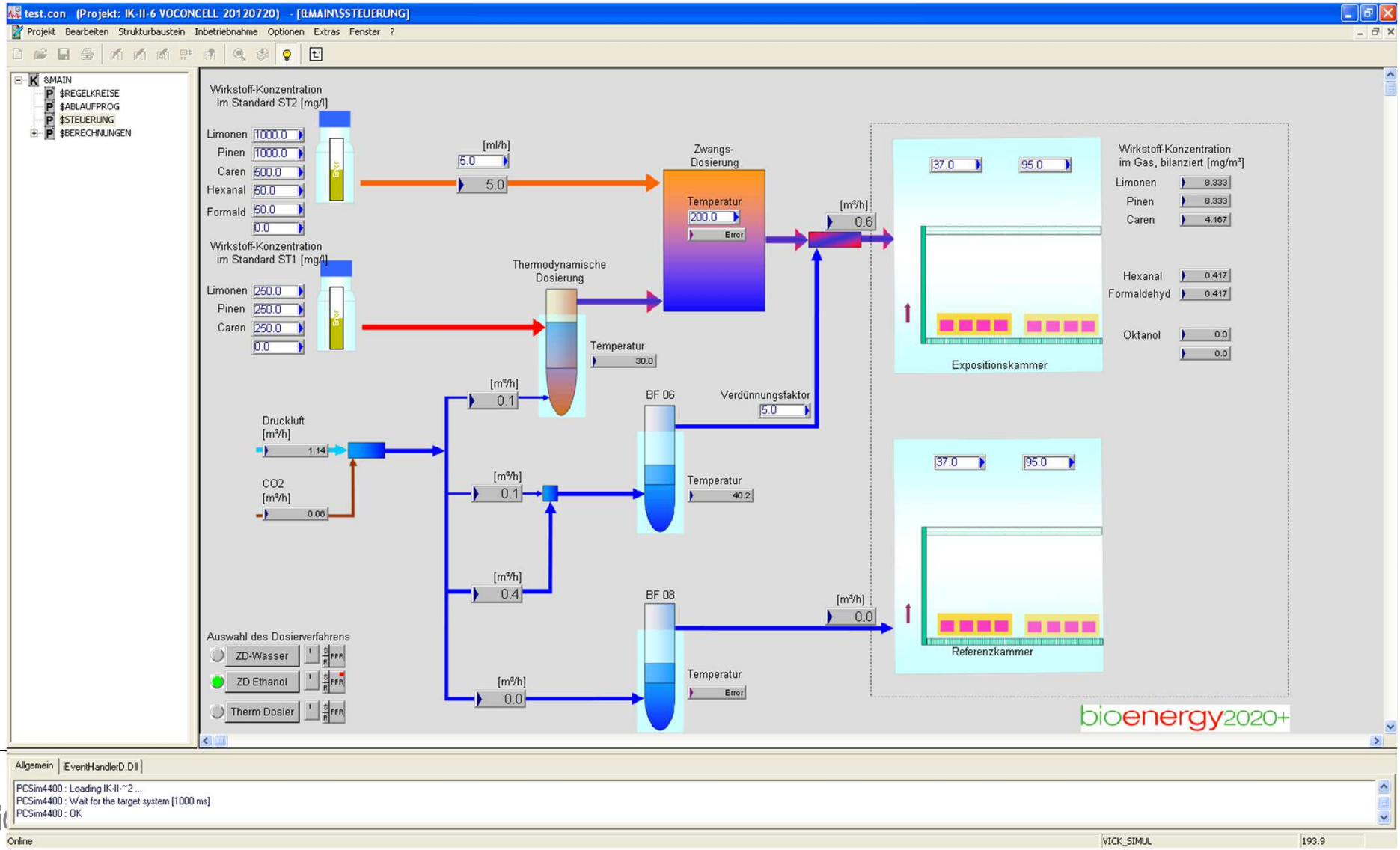
Barbara system for test gases in cell- based toxicology: control-cockpit



Barbara system for test gases in cell- based toxicology: GC-analysis in the system

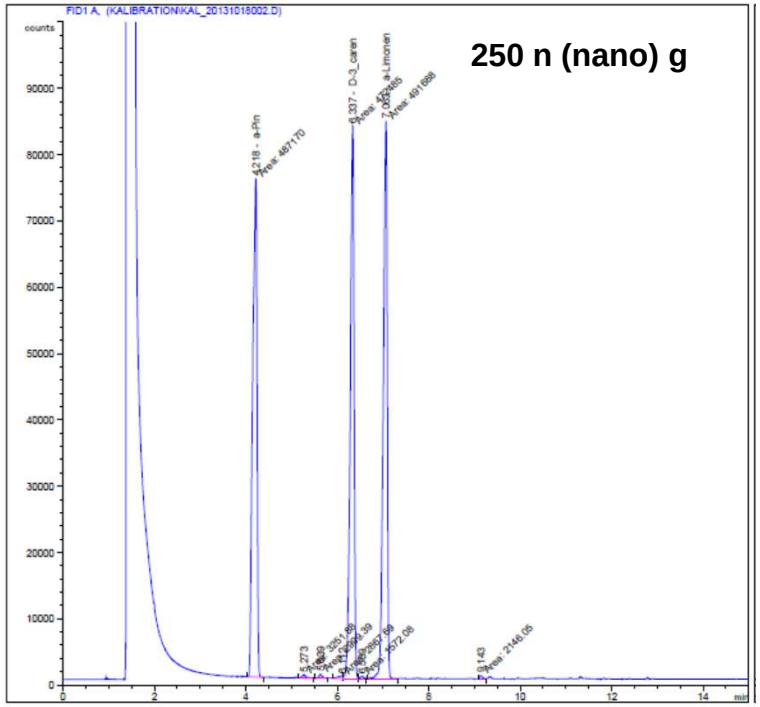
Vollautomation und Ergänzung einer Labormaschine

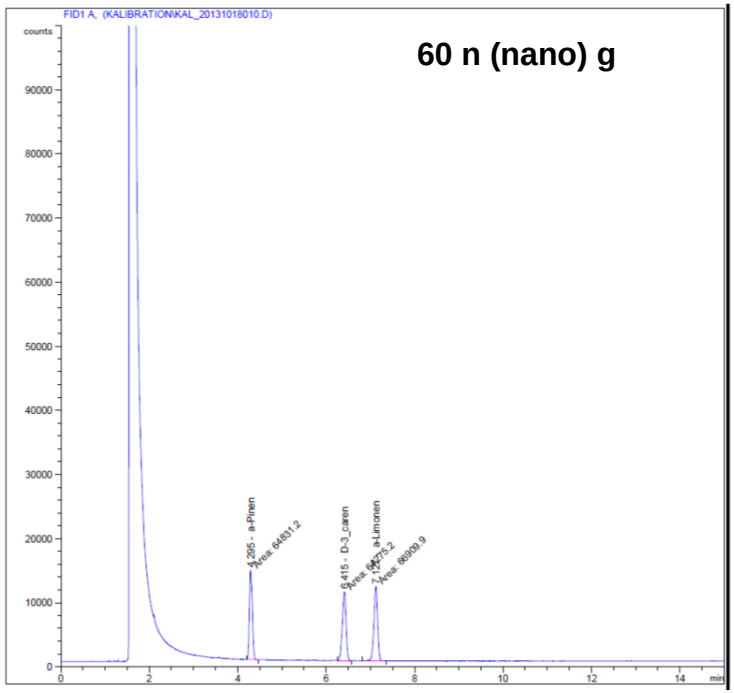
Messgasleitungen und Messgaspumpe

Vorderansicht GC-Ofen mit Ventilbox-Aufbau

Rückseite: elektrische Anspeisung und Anbindung BARBARA (Prozessleittechnik)

Barbara system for test gases in cell- based toxicology: GC-analysis in the system



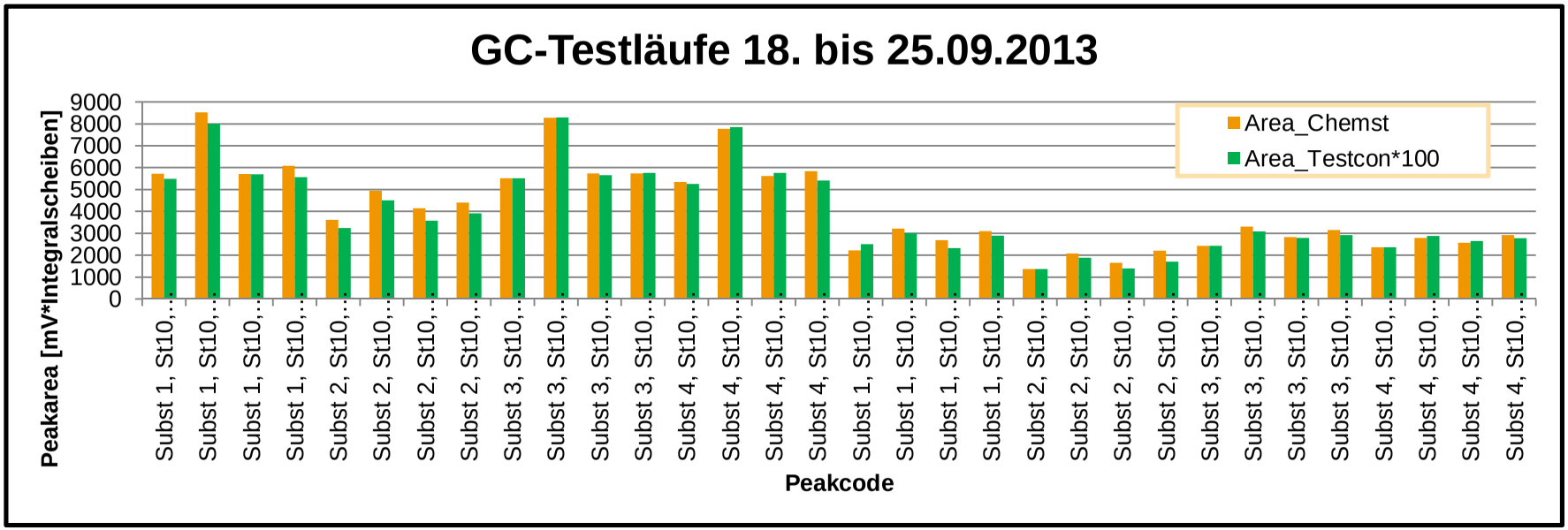


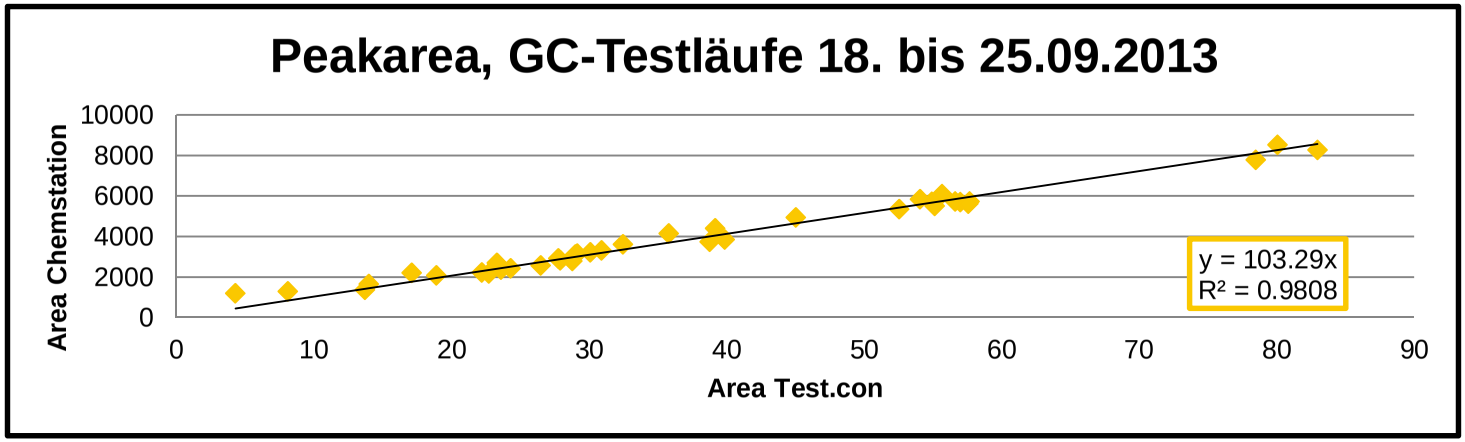
Terpene ST 10 / 100/ 500, incl. typischem Anteil von Wasser*)

**) auf das Wasser des Messgases der Ventilschaltung umgerechnet.*

Kalibration 10/2013 vor Auslieferung

Barbara system for test gases in cell- based toxicology: GC-analysis in the system





Barbara system for test gases in cell- based toxicology: mobile and nice