bioenergy2020+

Concept of round robin and host site activities

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innovations
kompetenz

Multistage RoundRobin
Disc. (8.03.2013)

Stage 1

- Internal Test of each single player
- E.g. method in house with reference system compared

⟷

- CEN/TS 15439
- Testgas generators

Stage 2

- **Testsamples o**f each sample
- Participant can receive sample (GC/HPLC)/100ml grav. CEN/TS,…

⟷

- Statistic result assessement

Stage 3

- On test sites with real plants
- Parallel sampling/measurements/final analysis
- Observing/samples (liquid/SPE)/active sampling

⟷

- Statistic result assessement

Necessary conditions to do the round robin

Hostsite

- Stable and controllable plant
- Sufficient number of sampling ports
- Technological infrastructure (location, energy supply, mechanical support, safety)
- Operation of the plant
- Sufficient preparation & organisation of the location

- Stability in operation & flexible assistance

Mobile participant

- Sufficient equipment
- Well prepared equipment setting
- Well trained staff for installation, testing, sampling and measurement
- Well prepared workflow incl. sufficient logistics for sample transport
- Precise preparation on site and pre-testing

- Durability & flexible adaptation onsite

Early enough planing and preparation of the action including time schedule, technical equipment and financing.

Benefits: Multi instrument measurements and data analysis
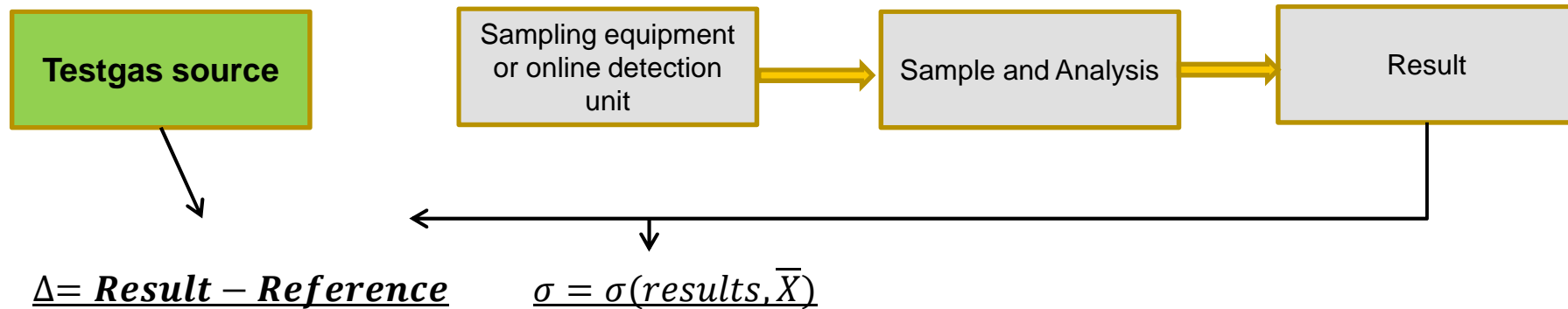- Will also take time to do and for discussion

Benefits: Comparison in procedural execution, reporting and the results.
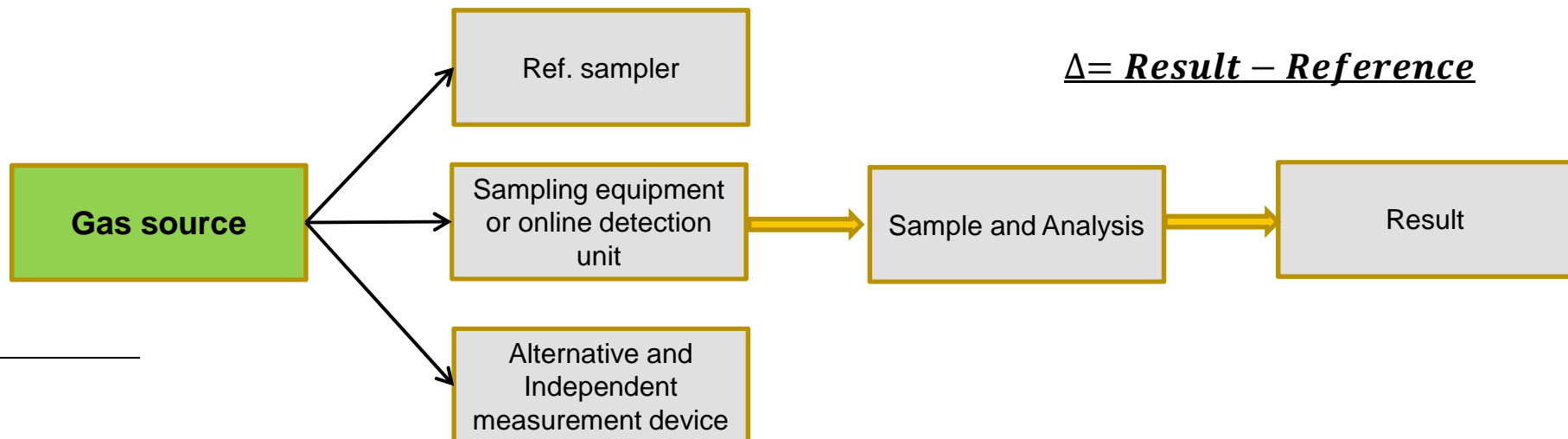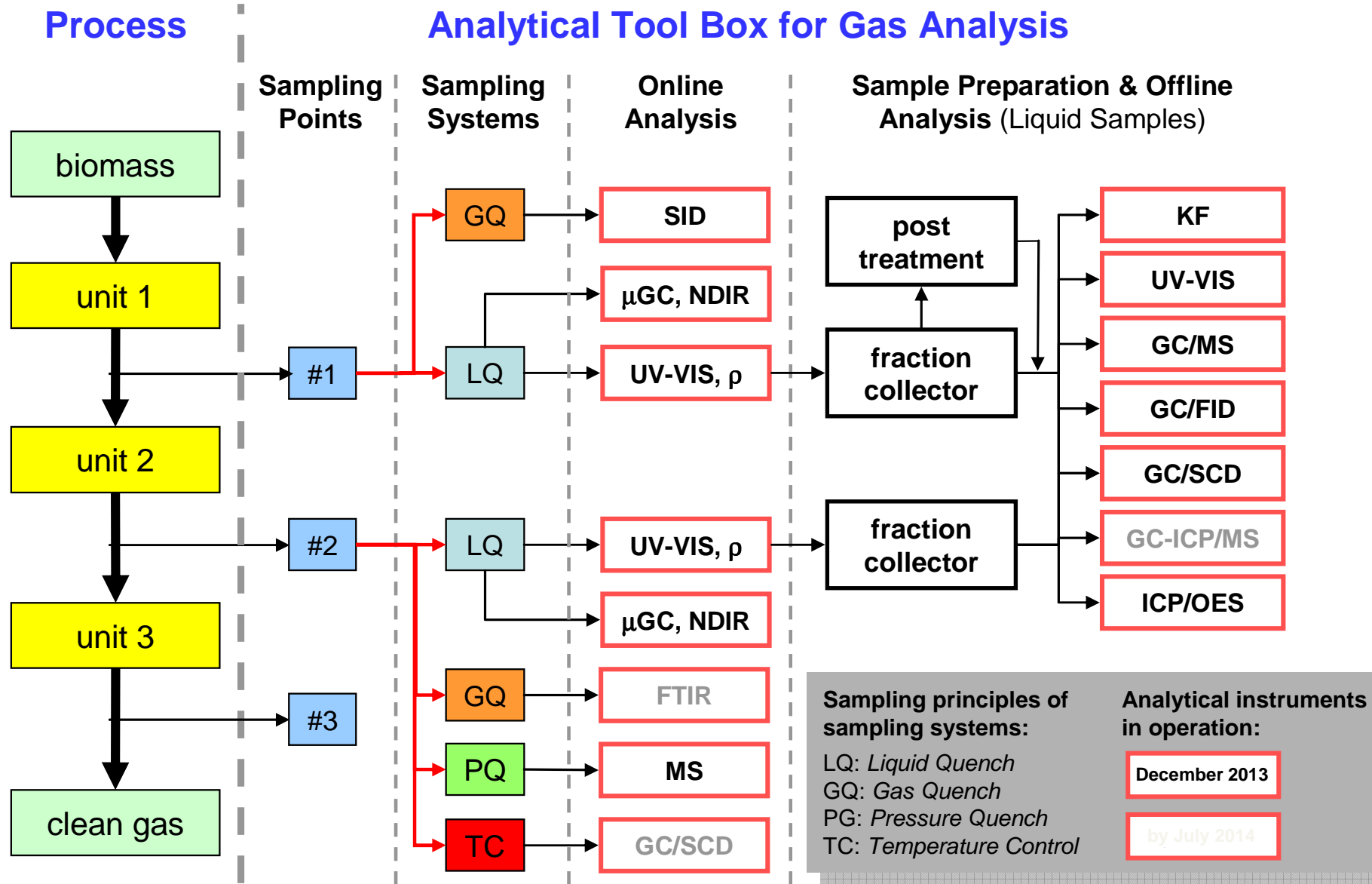- Needs precision for carrying out, reporting and will take time.

Quality measures
1. reference measurements for sampling

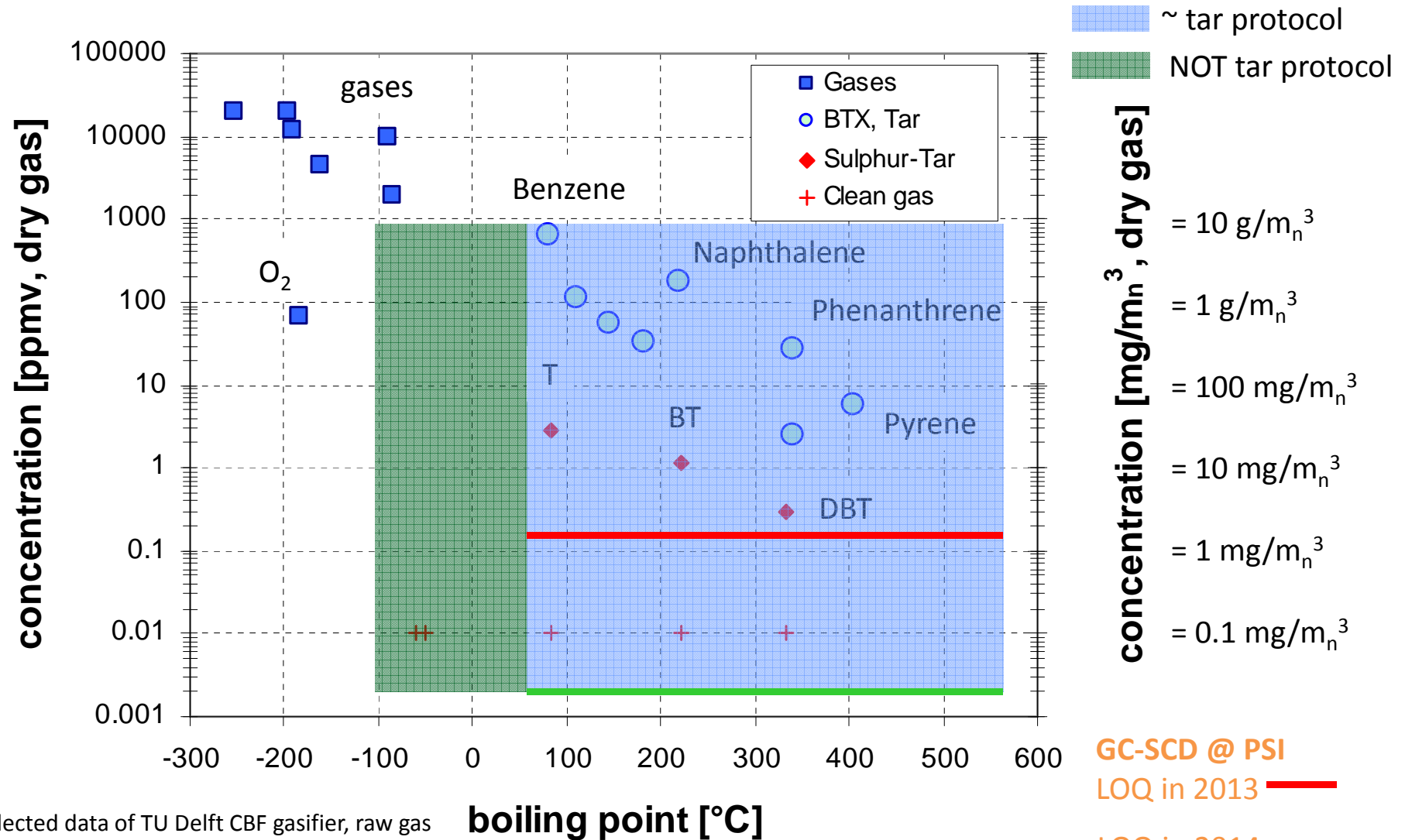**Test procedure 1:** a reference gas (cylinder) or a test gas generator is available.

```
┌──────────────┐      ┌──────────────────┐      ┌──────────────────┐      ┌──────────────┐
│ Testgas      │      │ Sampling equipment│ ──▶ │ Sample and       │ ──▶ │   Result     │
│ source       │      │ or online detection│    │ Analysis         │      │              │
│              │      │ unit              │      │                  │      │              │
└──────────────┘      └──────────────────┘      └──────────────────┘      └──────────────┘
```

$$\Delta = Result - Reference \qquad \sigma = \sigma(results, \overline{X})$$

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

```
                      ┌──────────────┐
                      │ Ref. sampler │            Δ= Result − Reference
                      └──────────────┘
┌──────────────┐      ┌──────────────────┐      ┌──────────────────┐      ┌──────────────┐
│ Gas source   │ ──▶  │ Sampling equipment│ ──▶ │ Sample and       │ ──▶ │   Result     │
│              │      │ or online detection│    │ Analysis         │      │              │
│              │      │ unit              │      │                  │      │              │
└──────────────┘      └──────────────────┘      └──────────────────┘      └──────────────┘
                      ┌──────────────────┐
                      │ Alternative and  │
                      │ Independent      │
                      │ measurement device│
                      └──────────────────┘
```

$$\Delta = Result - Reference$$

PSI's diagnostics toolbox: Status December 2013

Process

Analytical Tool Box for Gas Analysis

Sampling Points | Sampling Systems | Online Analysis | Sample Preparation & Offline Analysis (Liquid Samples)

biomass → unit 1 → unit 2 → unit 3 → clean gas

#1, #2, #3

GQ → SID
LQ → µGC, NDIR
LQ → UV-VIS, ρ
GQ → FTIR
PQ → MS
TC → GC/SCD

post treatment
fraction collector
fraction collector

KF, UV-VIS, GC/MS, GC/FID, GC/SCD, GC-ICP/MS, ICP/OES

Sampling principles of sampling systems:

LQ: *Liquid Quench*
GQ: *Gas Quench*
PG: *Pressure Quench*
TC: *Temperature Control*

Analytical instruments in operation:

December 2013

by July 2014

Tar - & sulphur protocol: Common basis

PAH: Polycyclic aromatic hydrocarbons   PASH: Polycyclic Aromatic Sulphur Heterocycles

Selected data of TU Delft CBF gasifier, raw gas

GC-SCD @ PSI
LOQ in 2013
LOQ in 2014

Sample treatment and on-/offline analysis
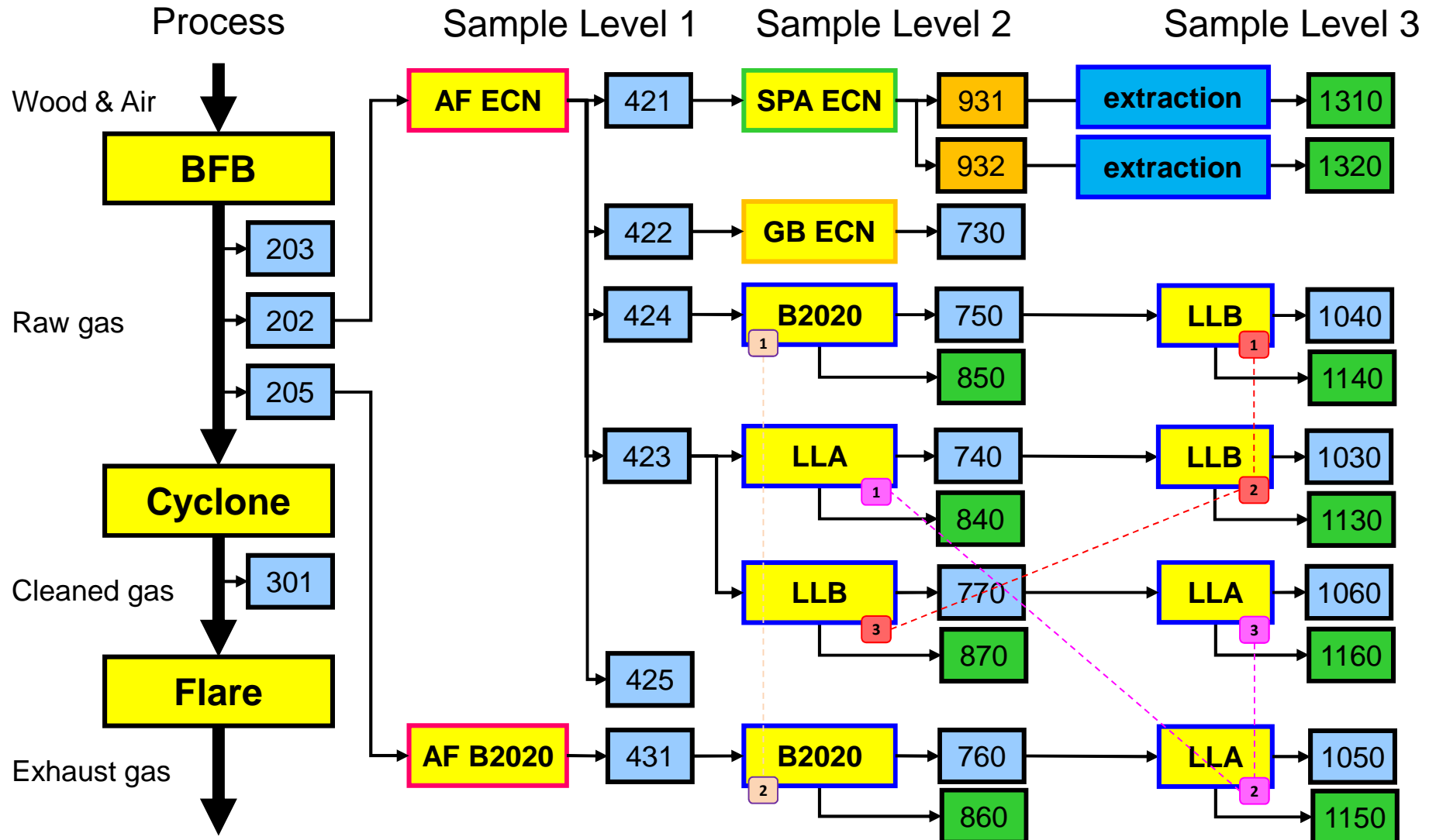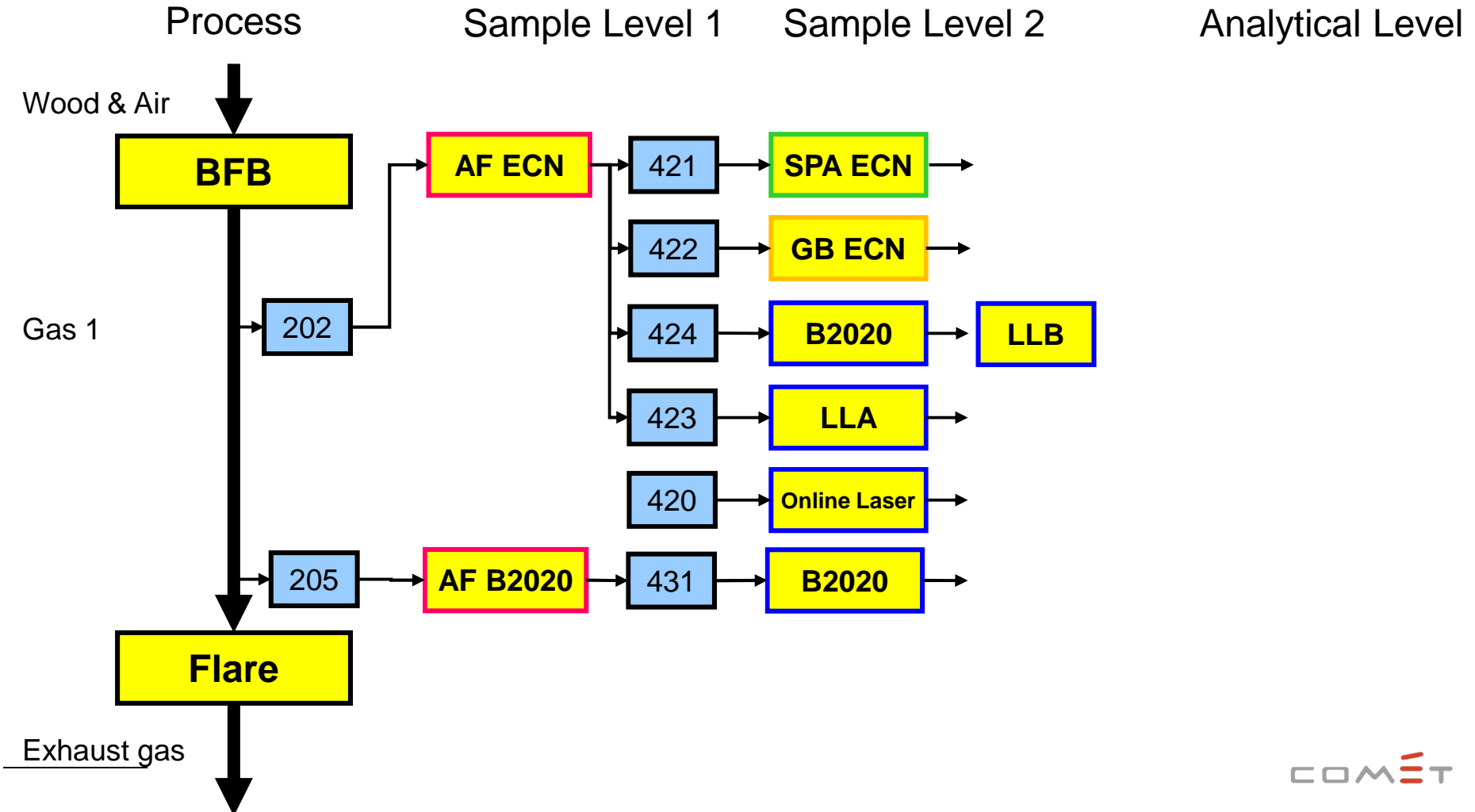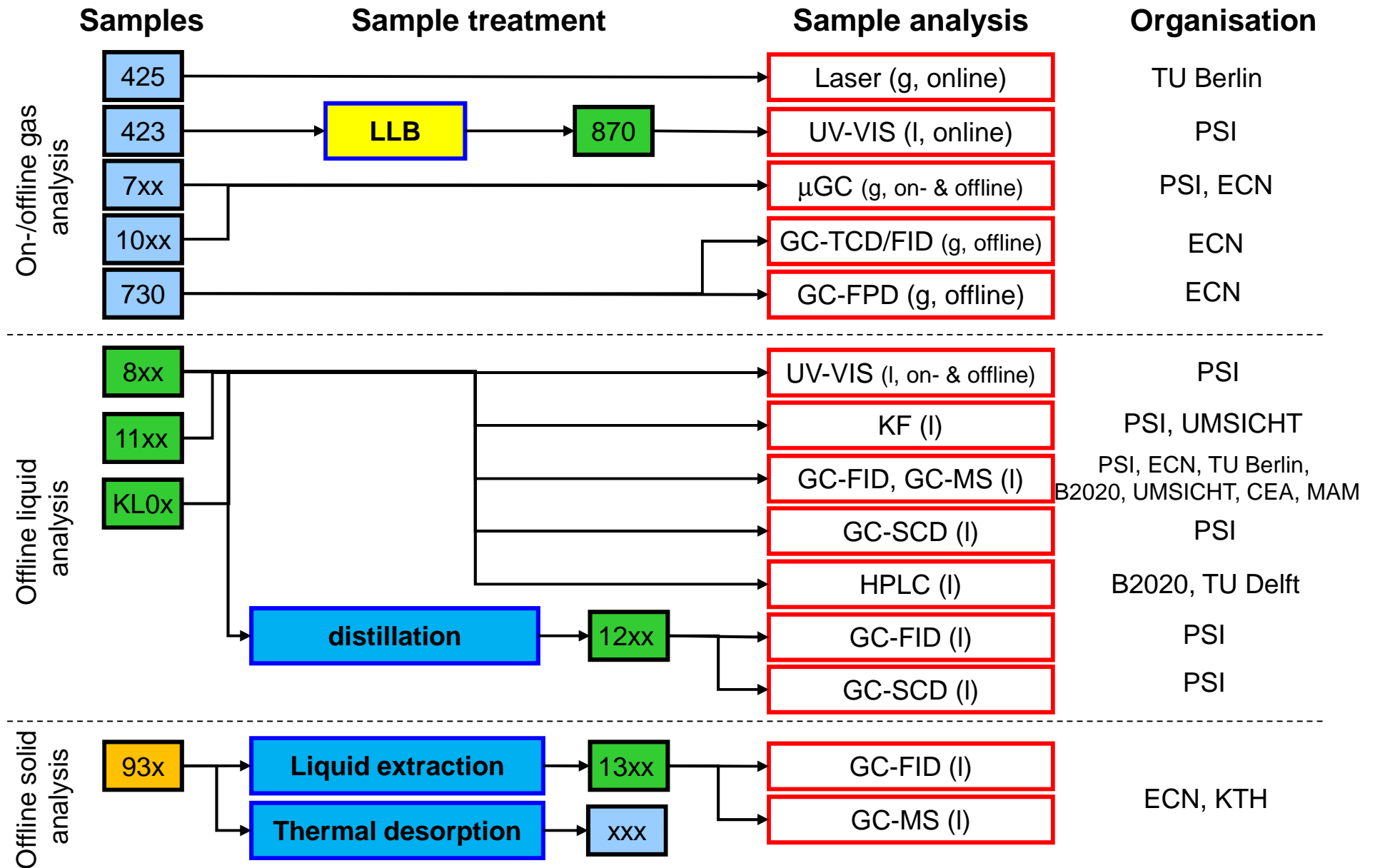
BRISK

Example of GC/FID
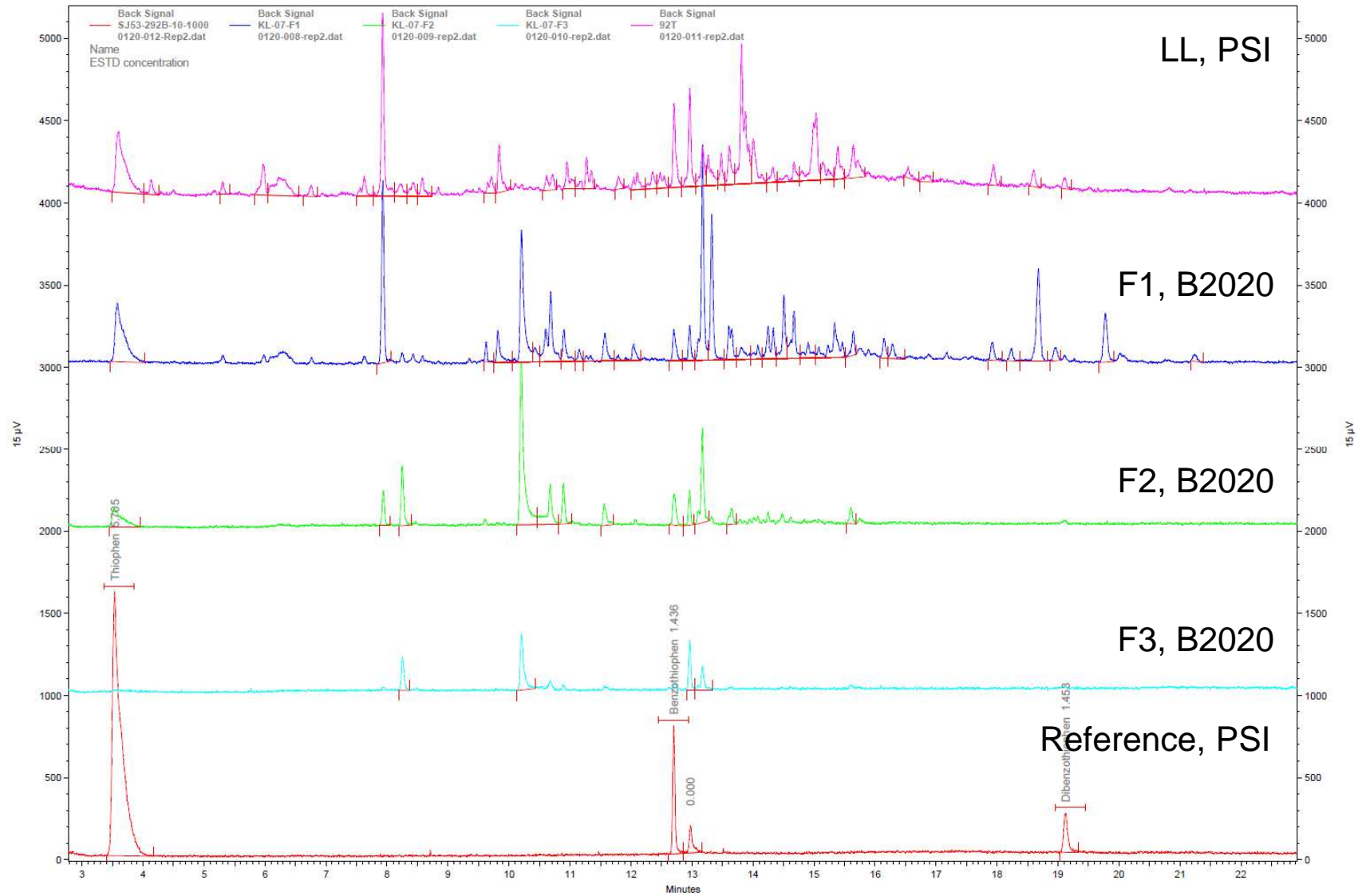chromatogram of sample
291T, without further
treatment, measured at PSI

Sampling time:
17:00 – 17:30 h

870
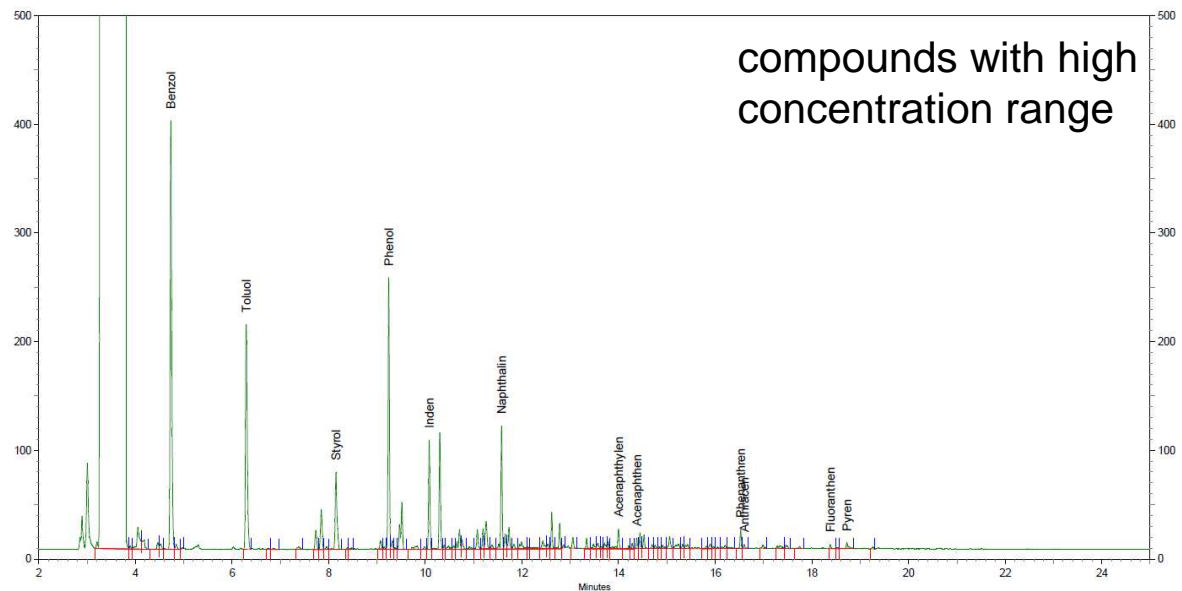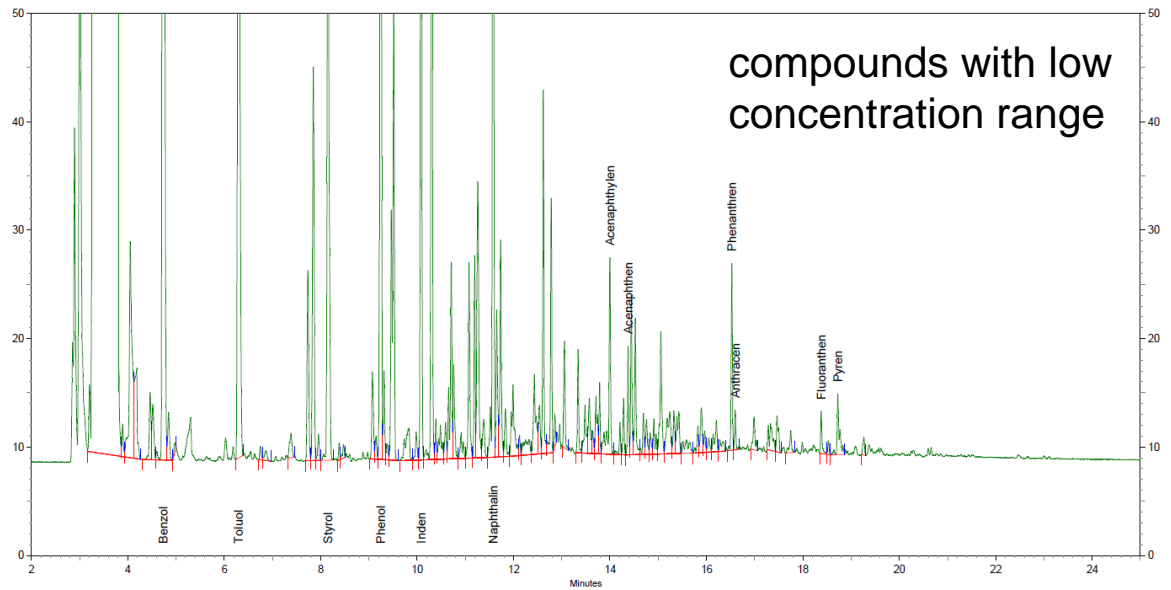
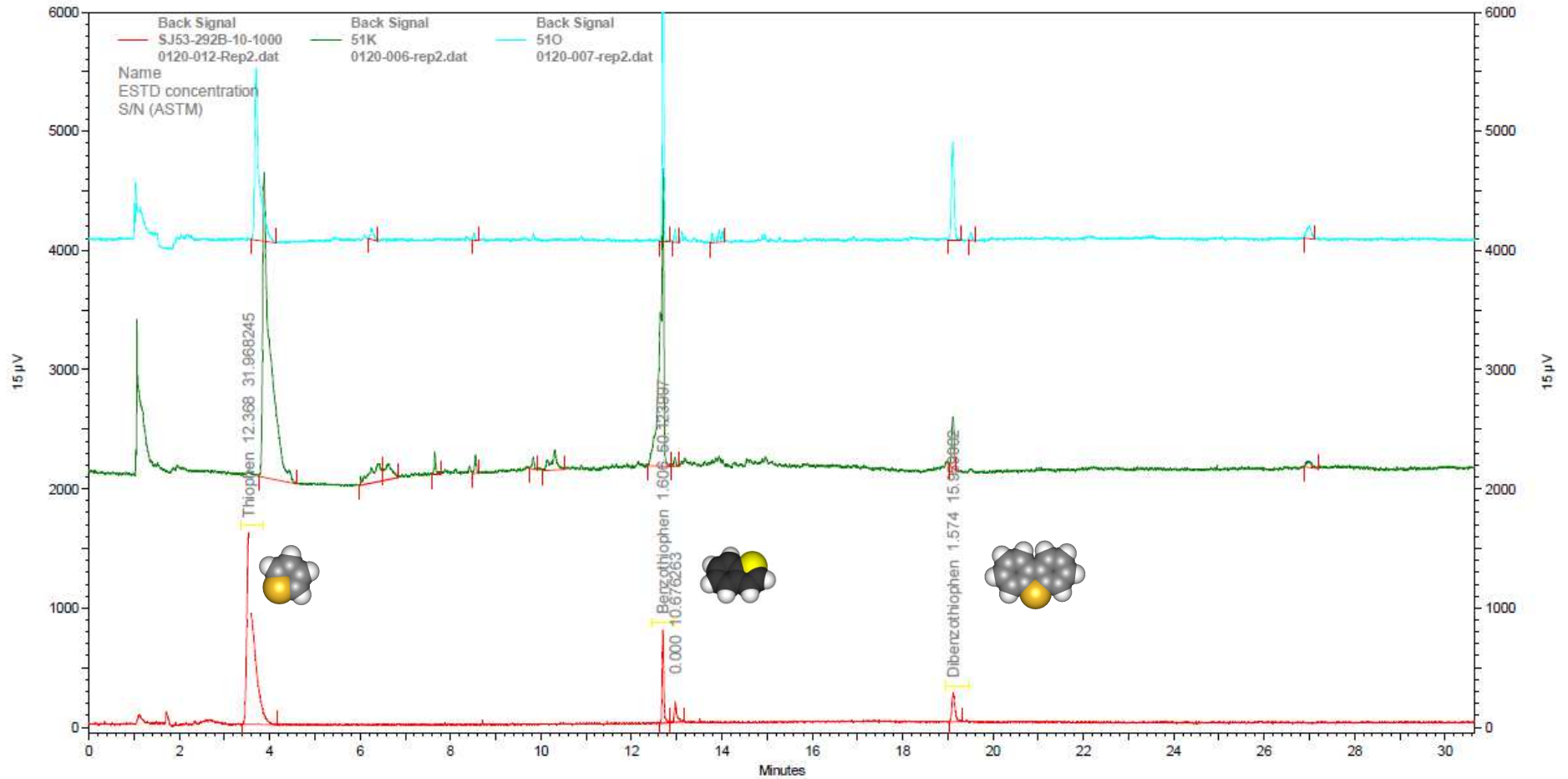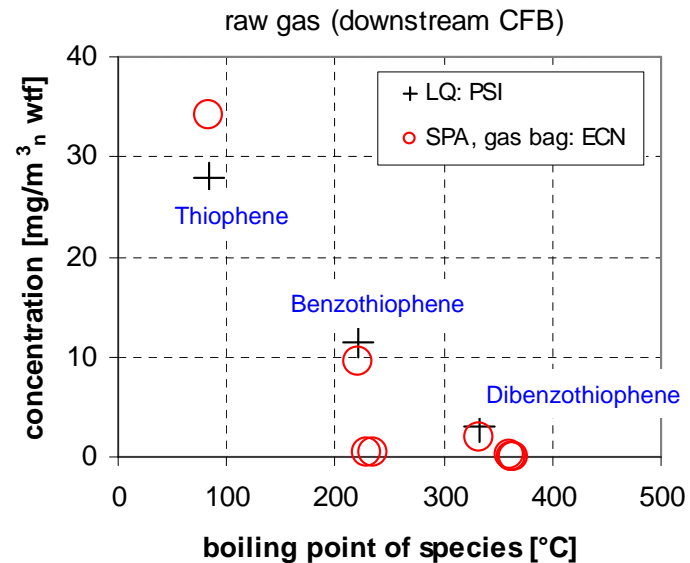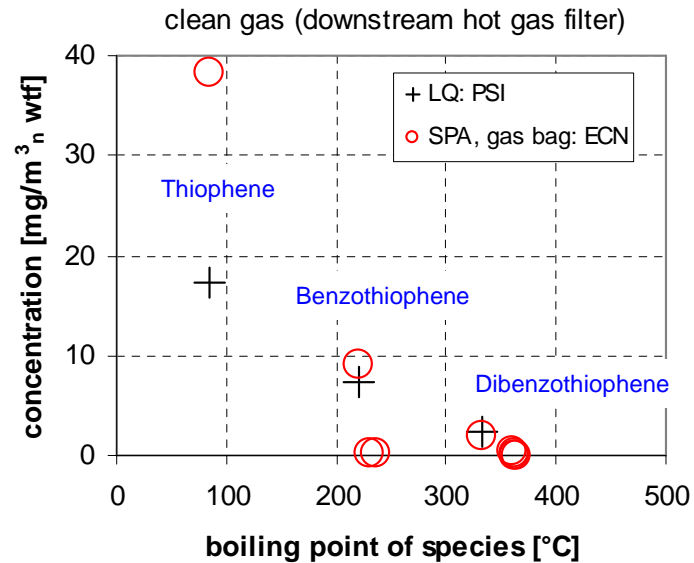BRISK GC-SCD: Comparing two different sampling systems

Post treatment of liquid samples (distillation)

Material flow

Sample «as received» → distillation 1

distillation 1 → Sample «distillate 1»

distillation 1 → distillation 2

distillation 2 → Sample «distillate 2»

distillation 2 → Solid ~ "gravimetric tars"
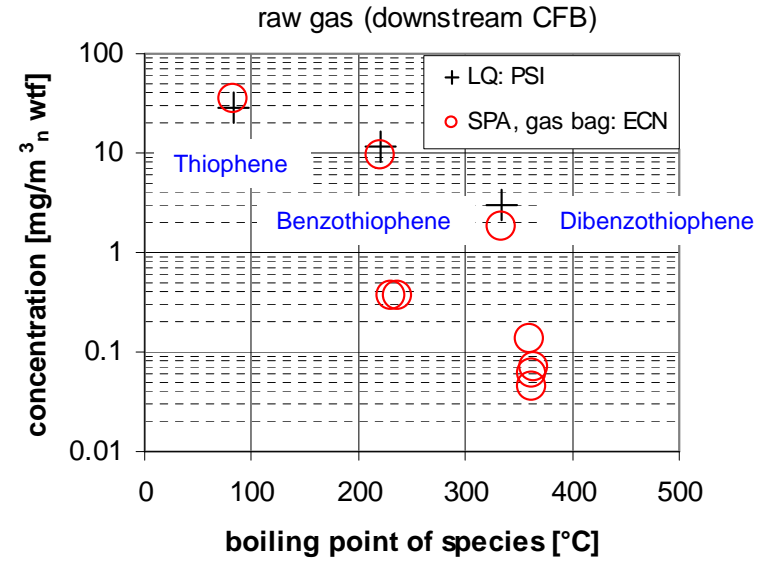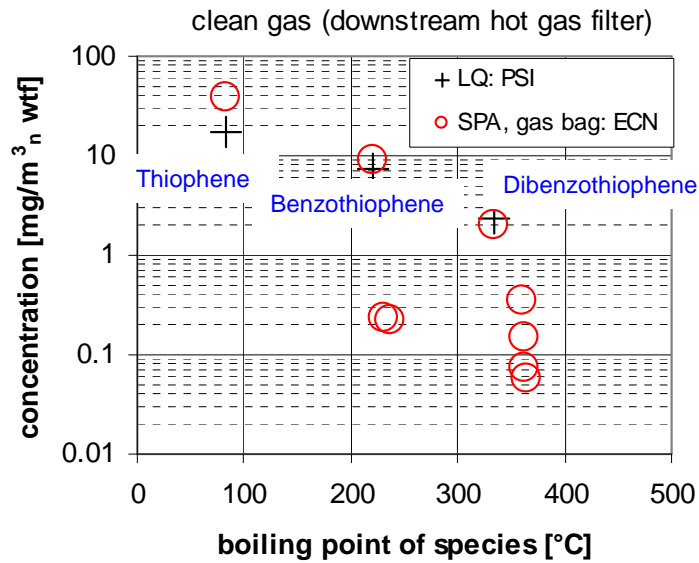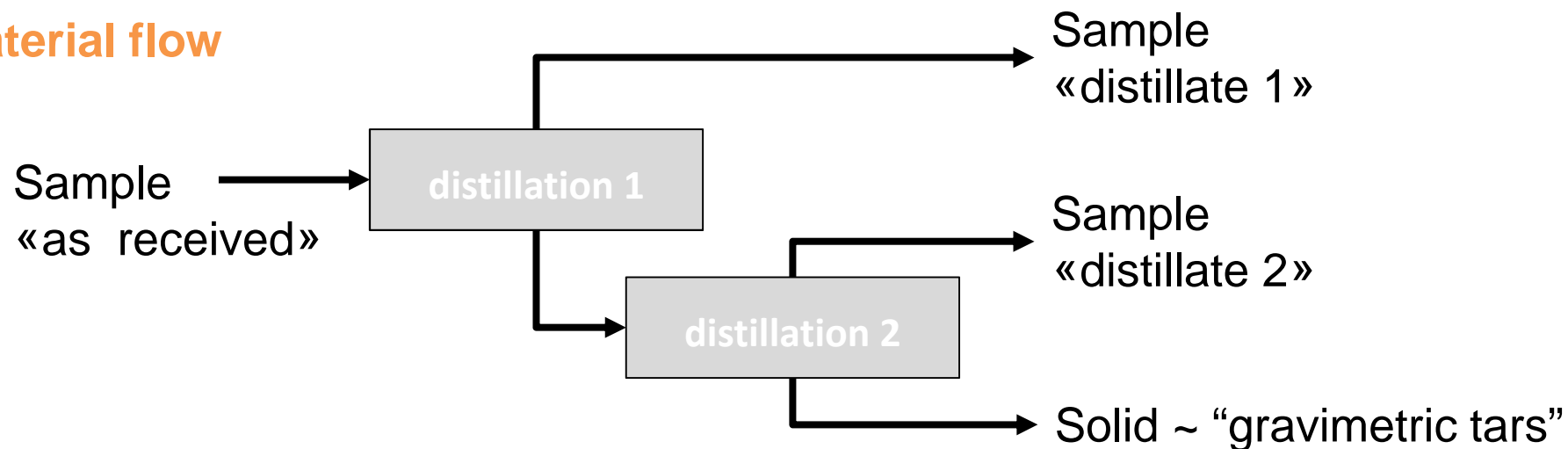
Set up

Kugelrohr

Kugelrohr (German for "ball tube") is a short-path vacuum distillation apparatus

1 Heating cage
2 Bulb containing item to be distilled
3 Cooling bath containing ice
4 Vacuum outlet and electric motor
   (to rotate ball-string)

a) Sample «as received»

b) Sample «distillate 1»

c) Sample «distillate 2»

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Mobilised Equipment Bioenergy2020+ *for RR Hostsite-visit* *‚Tar' (BTXE+PAH)*

- trace heating, adapted
- sample line in PTFE dm 12 mm o/ 10 mm i
- PTFE-probe not heated
- activated char coal
- silica gel
- flow rate display
- control valve
- ball valve
- PI
- FI
- drain
- cooling unit (-20°C)
- pump
- volume measurement
- cooled double jacket flasks for organic parameters
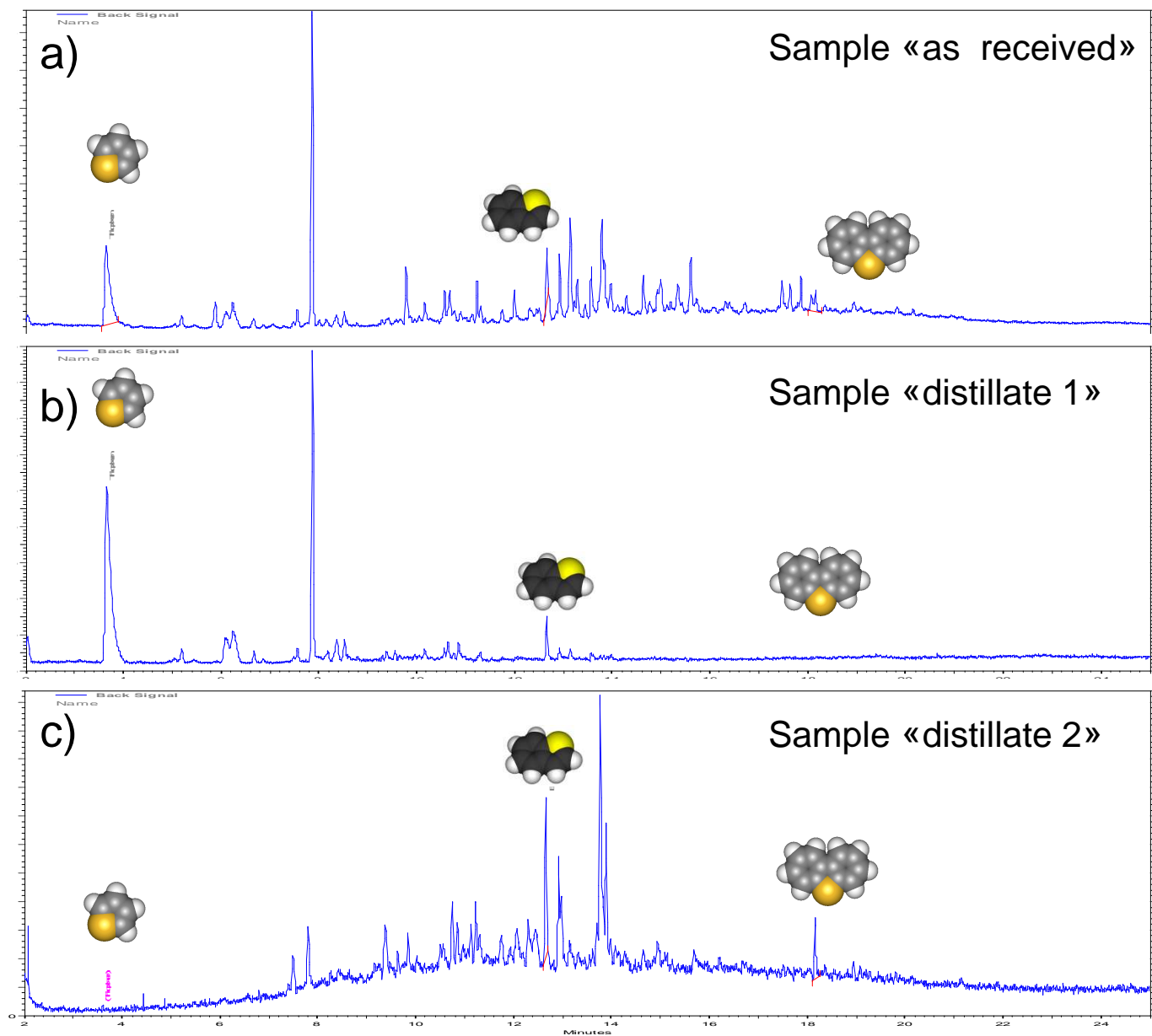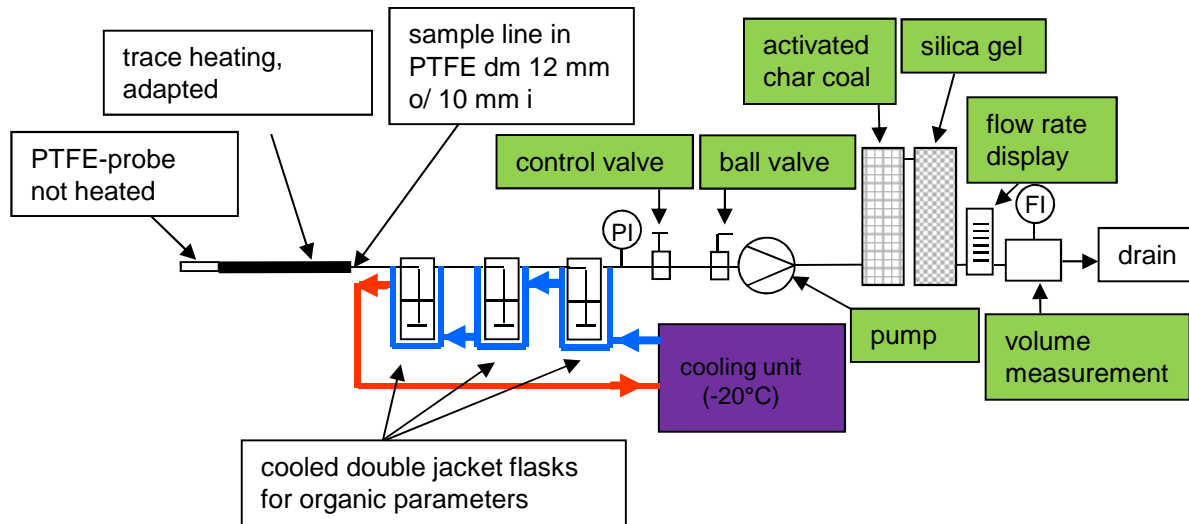
- **probe:** PTFE, glass
- **heated filters:**
- **absorption columns:** cooled (-20°C)
- **Optional delivered to PSI**
  - **pump:** membrane pump
  - **gas drying/cleaning:** silica, activated carbon
  - **volume detection:** diaphragm gas-meter

Equipment suitable for mobile ACTION ➡

Optional available

Not train-ransportable

1 train delivered

1 train delivered

BE Equipment

Folie 16

Example for result

RT	Substanz	xquer	sigma	xquer	sigma
[min]	[-]				
1,624	Benzol	2.731,7	117,6	2.581,2	314,6
2,181	Toluol	1.113,4	68,9	1.254,6	164,1
3,281	Ethylbenzol	79,4	7,0	105,4	3,3
3,413	m+p-Xylol	166,5	9,0	184,6	15,6
3,864	o-Xylol	331,1	22,5	240,5	226,6

Example for result

RT	Substanz	xquer	sigma	xquer	sigma	
[min]	[-]					
10,815	Naphthalin	Sampling point 424 185,8	32,2	102,1		70,5
15,325	AceNapthen	4,13	2,05	11,43		1,15
17,089	Fluoren	22,81	8,40	14,54		1,44
20,587	Phenanthren	28,88	8,64	25,72		10,30
20,779	Anthracen	6,37	0,51	13,26		6,25
26,889	Fluoranthen	34,98	11,65	93,70		52,87
28,170	Pyren	4,96	0,53	13,73		9,40
36,758	Chrysen	-	-	0,78		0,78
37,029	Benz(a)anthracen	-	-	-		-
44,509	Benz(b)fluoranthen	-	-	-	■ 424-e	-
44,688	Benz(k)fluoranthen	-	-	3,61	■ 424-d	3,61
46,545	Benz(a)pyren	-	-	-	■ 424-c	-
53,566	Indeno(1,2,3-cd)pyren	-	-	-	■ 424-b	-
53,925	Dibenzo(a,h)anthracen	-	-	-	■ 0-a	-
54,961	Benzo(ghi)perylen	-	-	2,62		2,62

Further round robin

Hostsite

- KIT
- ECN

- Open for others

Mobile participant

- 1
- 2
- 3
- 4

Early enough planing and preparation of the action including time shedule, technical equipment and financing.

Benefits: Multi instrument measurements and data analysis
- Will also take time to do and for discussion

Benefits: Comparison in procedural execution, reporting and the results.
- Needs precision for carrying out, reporting and will take time.

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 $\pm$ σ.
e.g. an analysis delivers the **quantification**, if it exeeds 9-times the $\pm$ σ .

Or LOQ ~3*LOD

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.