

EMISSION MONITORING IN INDUSTRIAL PROCESSES

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SINTEF Industry

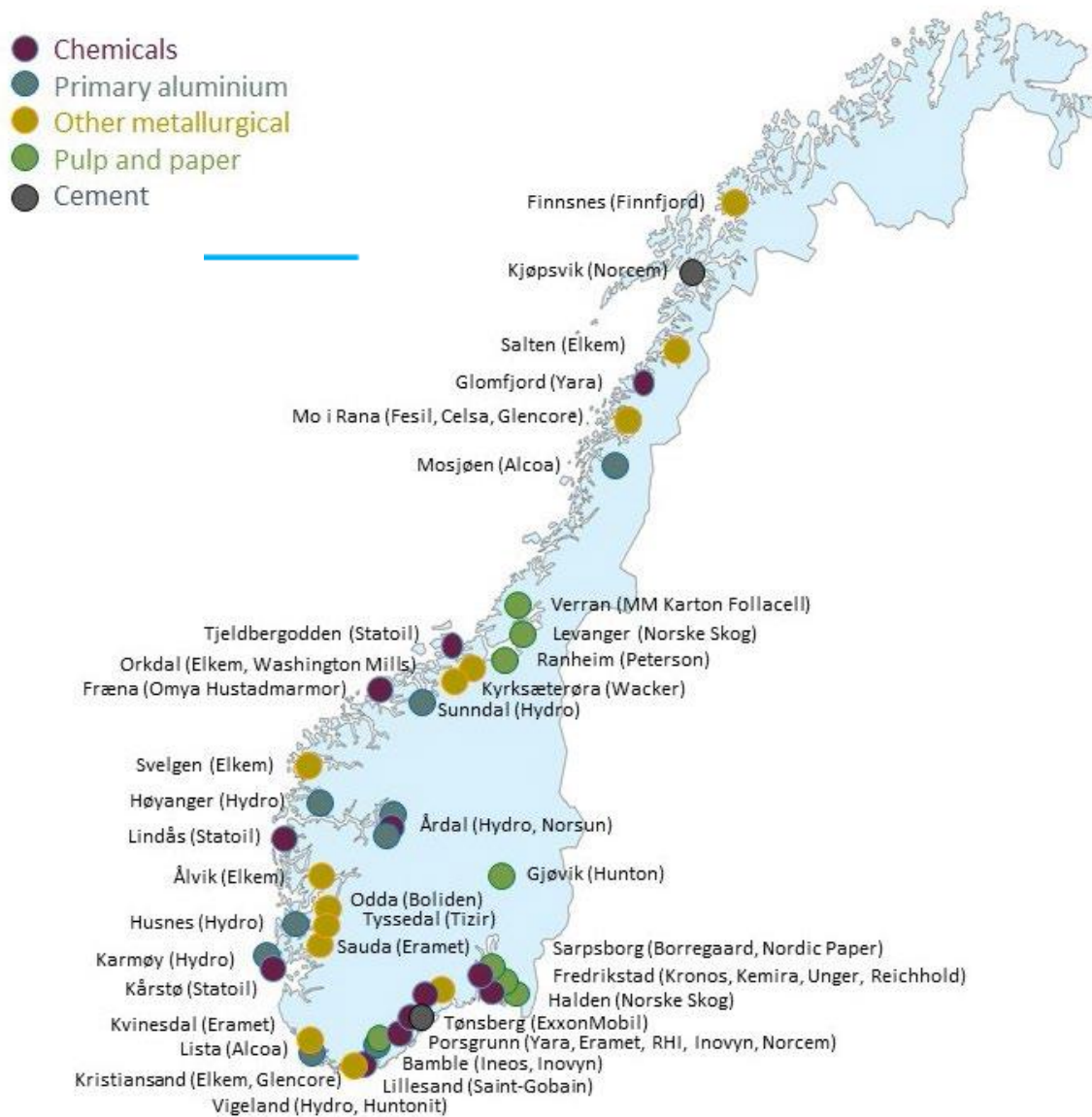
Outline

Introduction

- Purpose of emission monitoring – Instruments and examples

Measurement planning

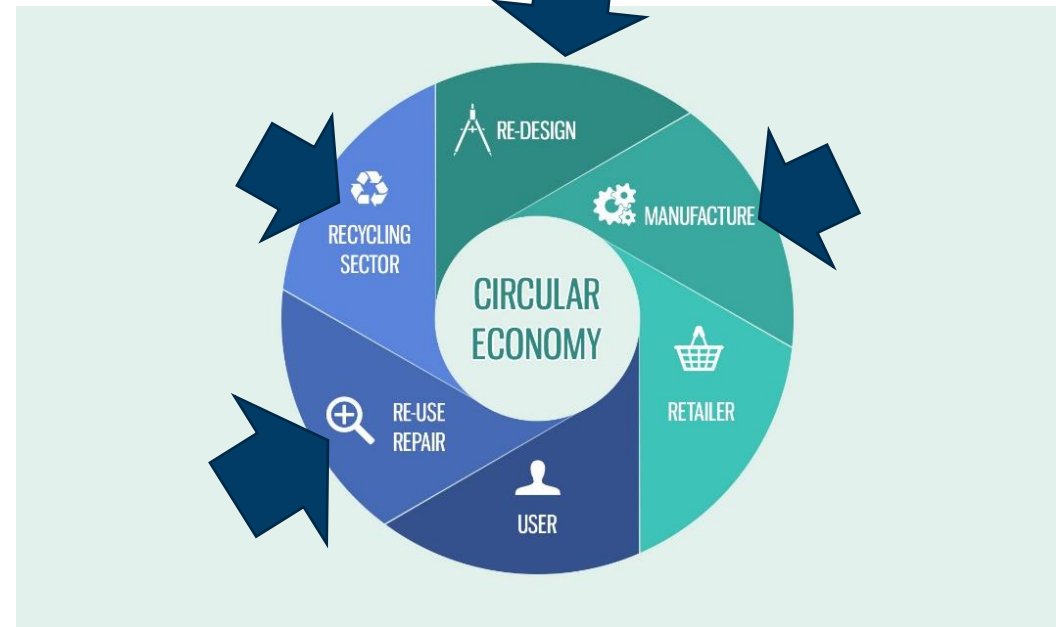
- Use basic principle - Design and Risk access – Lessons learned
- Measurement systems - Challenges



Norwegian Process Industries

toward low carbon - circular economy

Minimizing resource input, waste, energy and emission leakage



Introduction

Emissions: "Pollution" generated through industrial activities

Emission data can be used

- to develop and verify process models
- to develop and integrate monitoring and control systems
- to improve the environmental performance of processes.

Convert waste streams to value

- Heat recovery (scaling)
- Rare earth metals recycling and emissions in off gas particles
- Power generation (CO and H₂ rich off-gas)
-

Gaseous and particulate emissions

Laboratory and field industrial applications

Common gases: CO, CH₄, CO₂, SO₂, NO, NO₂, H₂O, O₂, HCl, N₂O, COS, H₂, He, CF₄, HF and N₂

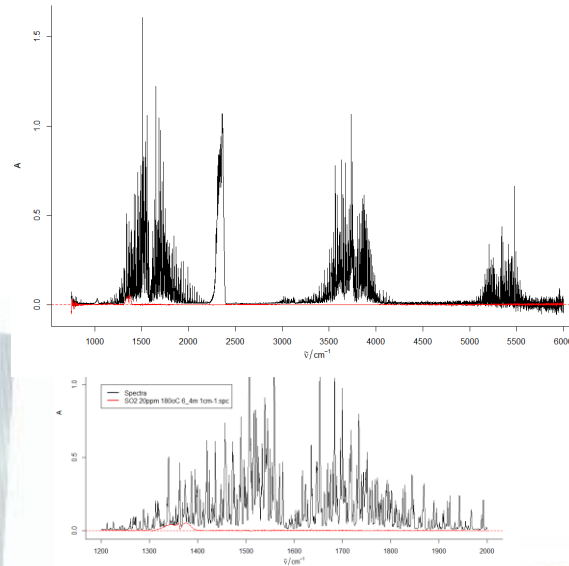
- Gas chromatography (GC)
- Mass Spectroscopy (MS)
- Fourier Transform Infrared Spectroscopy (FTIR)

Particulates and condensing phases

- Isokinetic sampling systems – Toolbox (Heavy metal, particles, condensates, organic compounds)
- Electric Low Pressure Impactor (in-situ / online particle distribution)

Fourier Transform Infrared Spectroscopy (FTIR)

atmosFIR / 204M
Combustion Gas Analyser



Component	Range 1 / mg/m3	Range 2 / mg/m3	Range 3 / mg/m3
CO	0 - 75	0 - 300	0 - 2000
NO	0 - 80	0 - 200	0 - 600
NO ₂	0 - 50	0 - 200	0 - 500
N ₂ O	0 - 50	0 - 100	
SO ₂	0 - 75	0 - 300	0 - 1275
NH ₃	0 - 15	0 - 50	
HCl	0 - 15	0 - 100	0-1000
HF	0 - 15	0 - 100	
CH ₄ (Methane)	0 - 15	0 - 50	0 - 1000
C ₂ H ₆ (Ethane)	0 - 15	0 - 50	0 - 100
C ₃ H ₈ (Propane)	0 - 15	0 - 50	0 - 100
C ₂ H ₄ (Ethylene)	0 - 15	0 - 50	0-100
HCHO (Formaldehyde)	0 - 15		
TOC (Indication only)	0 - 50	0 - 100	0-2000
H ₂ O	0 - 30%Vol	0 - 40%Vol	
CO ₂	0 - 20% Vol		
O ₂	0 - 20.9% Vol		



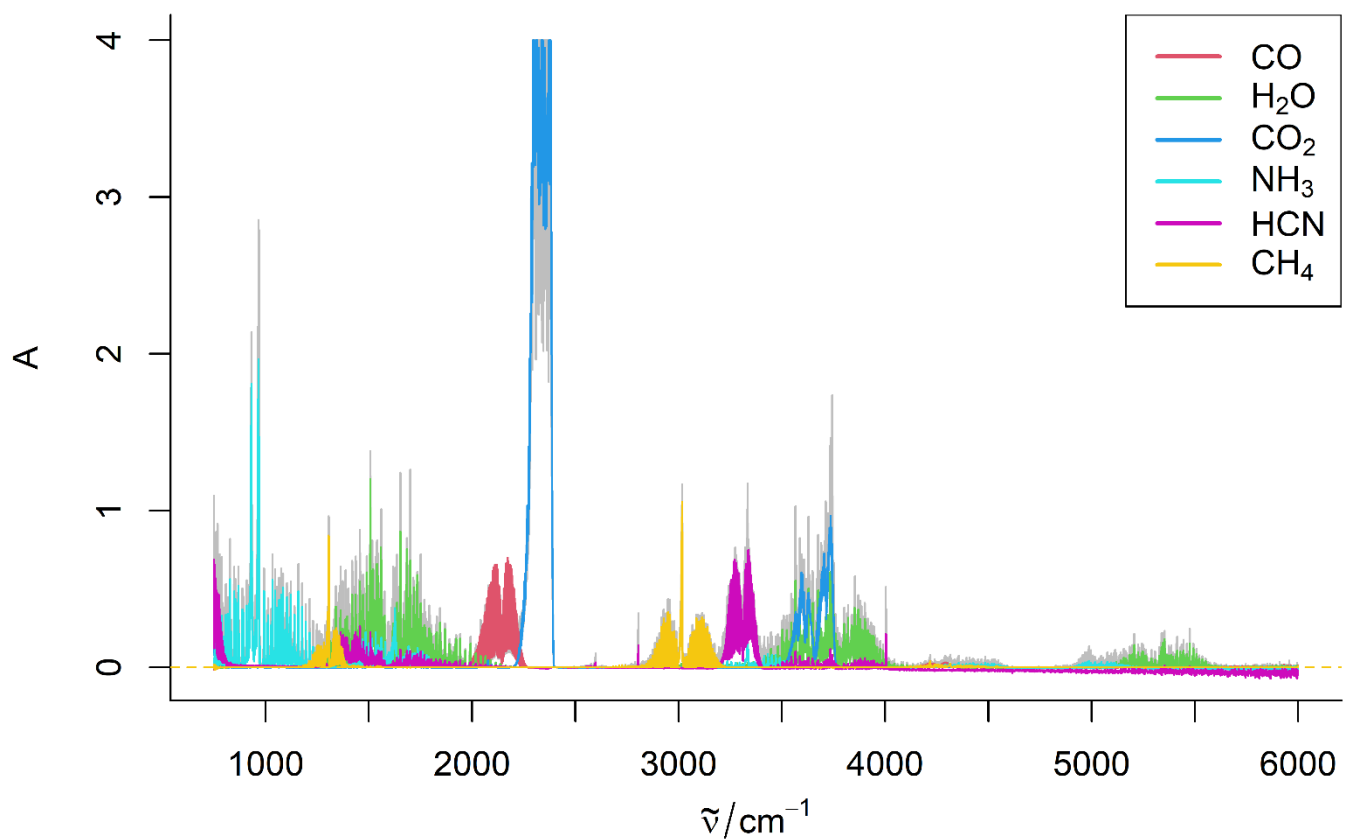
Component	Standard Range / mg/m ³	Extended Range / mg/m ³ *	Lower Detection Limit (LDL) / mg/m ³ **
CO	0 - 75 mCerts	0 - 18750	0.2
NO	0 - 200 mCerts	0 - 2000	0.9
NO ₂	0 - 200	0 - 2000	0.3
N ₂ O	0 - 100	0 - 1000	0.2
SO ₂	0 - 75 mCerts	0 - 30000	0.8
NH ₃	0 - 15 mCerts	--	0.1
HCl	0 - 15 mCerts	0 - 4000	0.3
HF	0 - 15	0 - 70	0.1
HBr	0 - 200	--	1.8
CH ₄ (Methane)	0 - 70	0 - 700	0.2
C ₂ H ₆ (Ethane)	0 - 50	0 - 1400	0.4
C ₃ H ₈ (Propane)	0 - 50	0 - 2000	0.3
C ₄ H ₁₀ (n-Butane)	0 - 50	0 - 300	0.9
C ₆ H ₁₄ (n-Hexane)	0 - 50	0 - 400	0.9
C ₂ H ₄ (Ethene)	0 - 25	0 - 1250	0.3
CH ₃ OH (Methanol)	0 - 70	--	0.4
HCHO (Formaldehyde)	0 - 20	--	0.3
C ₆ H ₆ (Benzene)	0 - 250	--	3.4
C ₆ H ₆ O (Phenol)	0 - 100	--	0.4
HCN	0 - 15	0 - 600	0.2
CCl ₄	0 - 200	0 - 1400	3.0
CS ₂	0 - 100	0 - 400	0.4
COS	0 - 50	--	0.05
CF ₄	0 - 40	0 - 600	0.05
SF ₆	0 - 65	--	0.05
TOC (Indication only)	0 - 50	0 - 2000	0.4
H ₂ O	0 - 40 % mCerts	--	<1000ppm
CO ₂	0 - 20 %	0 - 60%	<2ppm
O ₂ (via zirconia sensor)	0 - 20.9% mCerts	N/A	<0.4%

*Extended range is not fixed. This can be extended either by requesting extended analysis from Protea, or for smaller increases in range the user can span the system on their own gas cylinders.

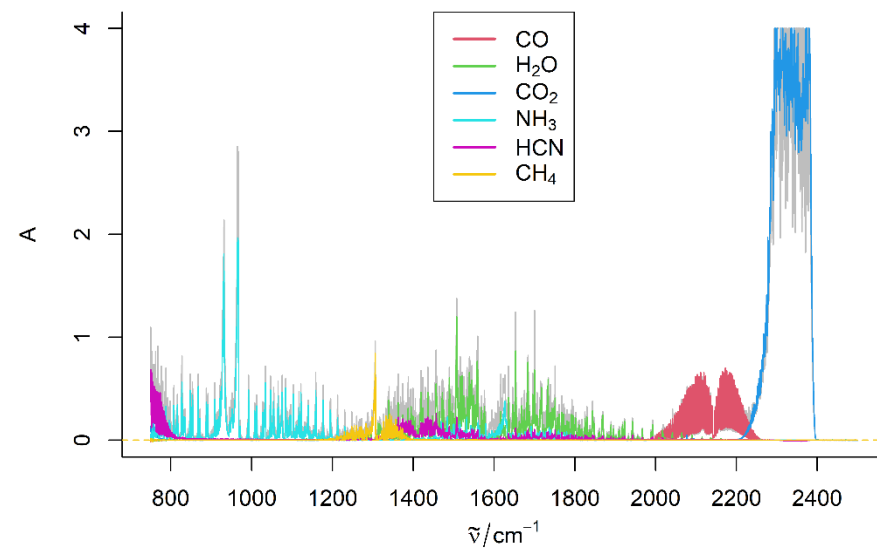
**The quoted LDL is for a ProtIR 204M FTIR gas analyser with standard optics. The LDL will vary with modifications and changes to the system.

FTIR Spectra

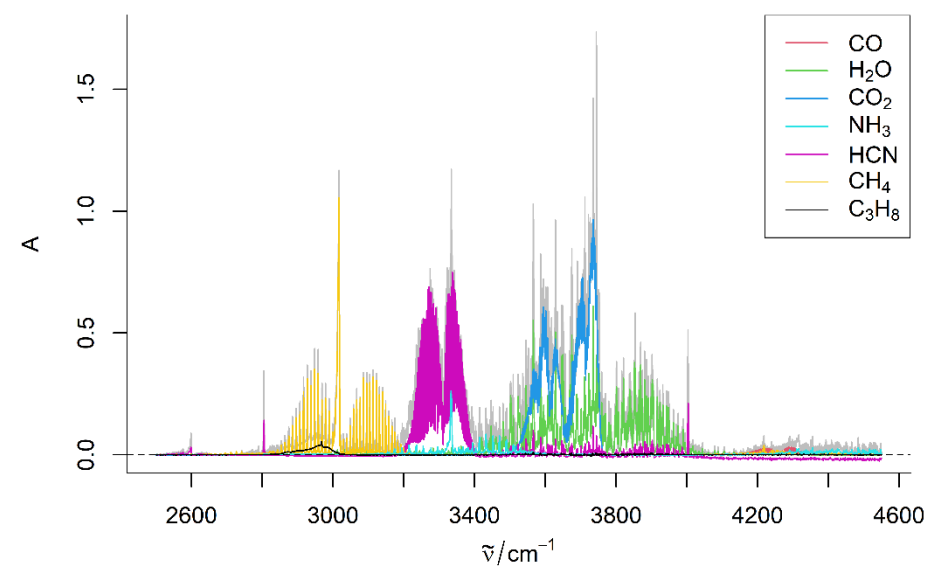
Spectrum 150



Spectrum 150

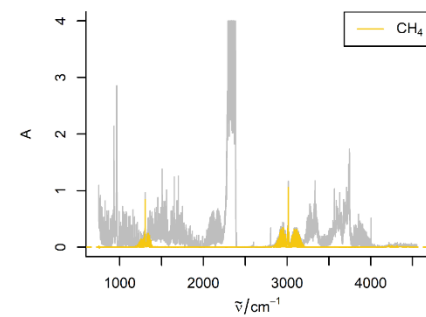
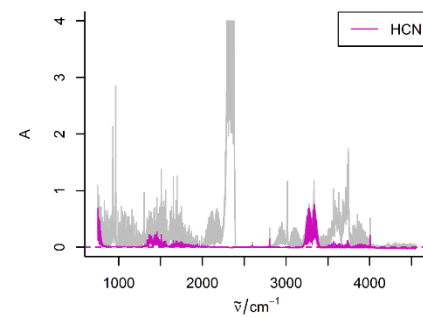
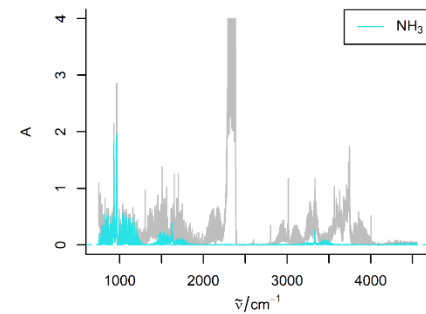
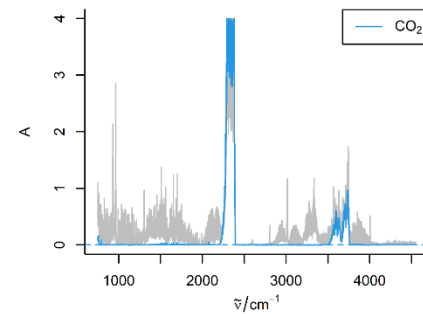
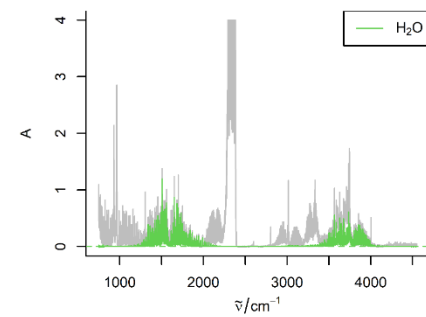
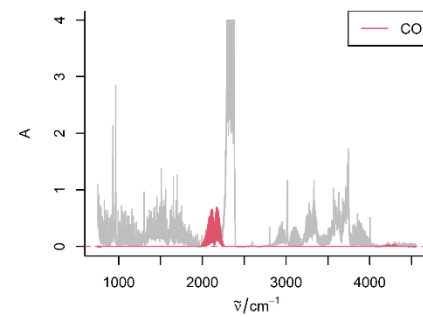
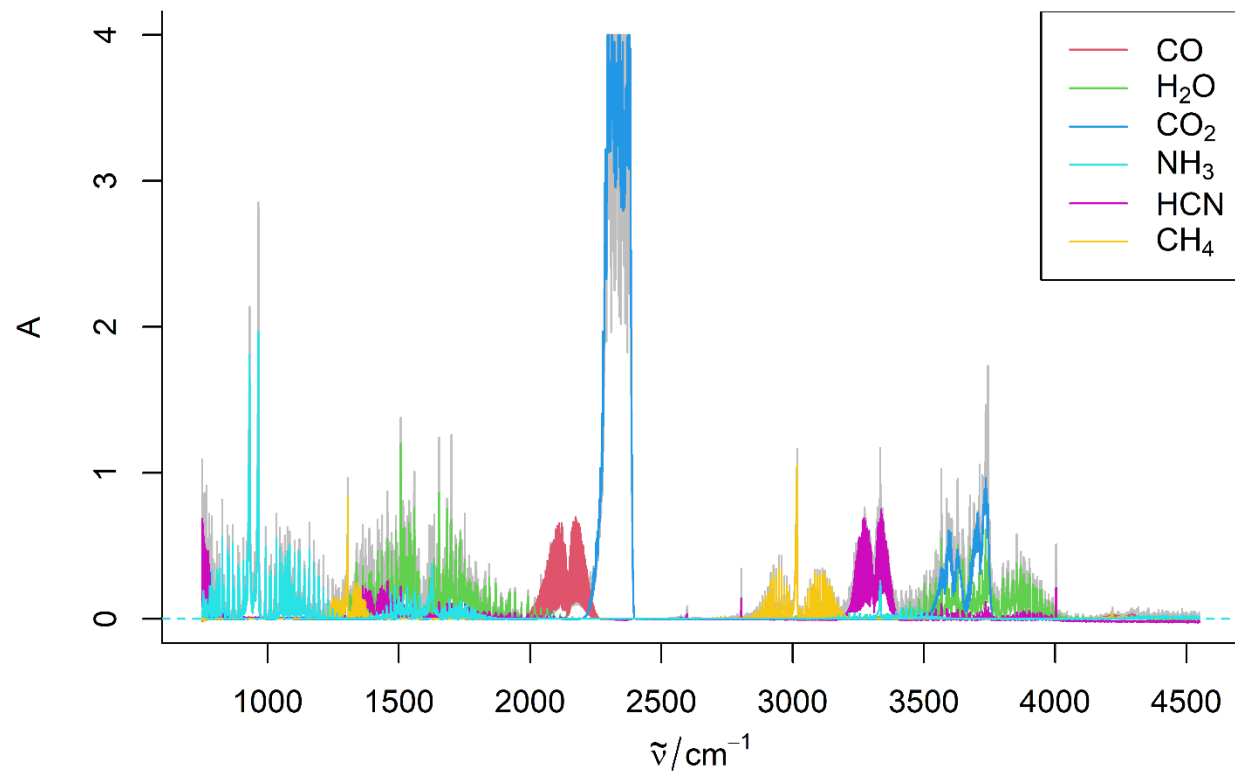


Spectrum 150

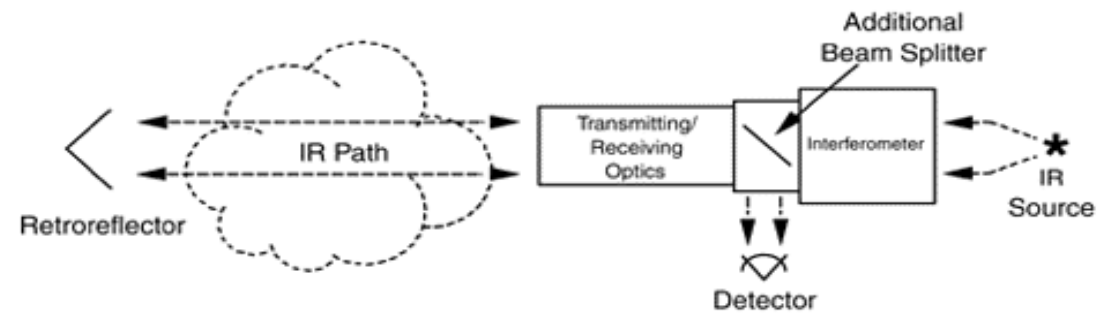


FTIR Spectra

Spectrum 150



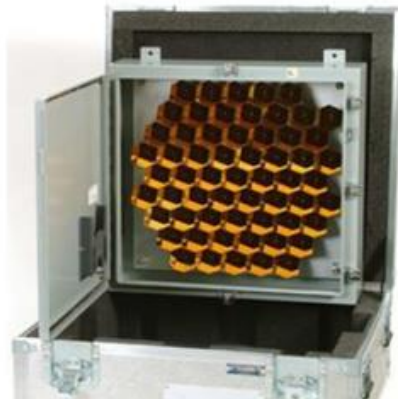
Open Path FTIR



Open-Path sensors, Supplier: ABB, FTIR (1.5—13.5 μm) measurement of a large range of chemical species simultaneously. Full atmospheric transmission spectrum within seconds.

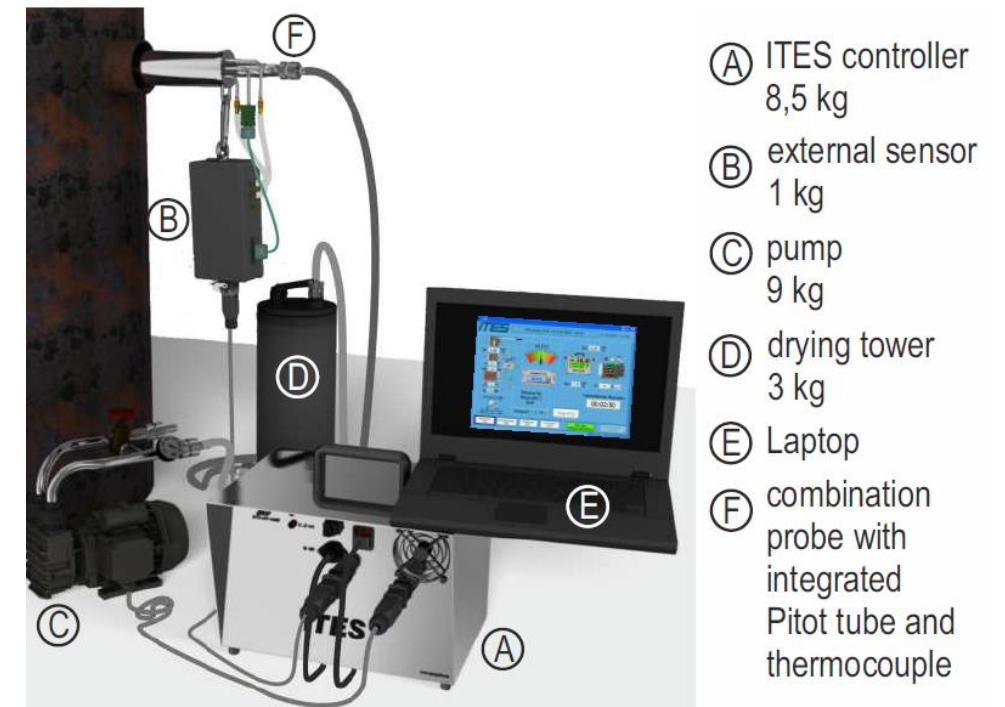
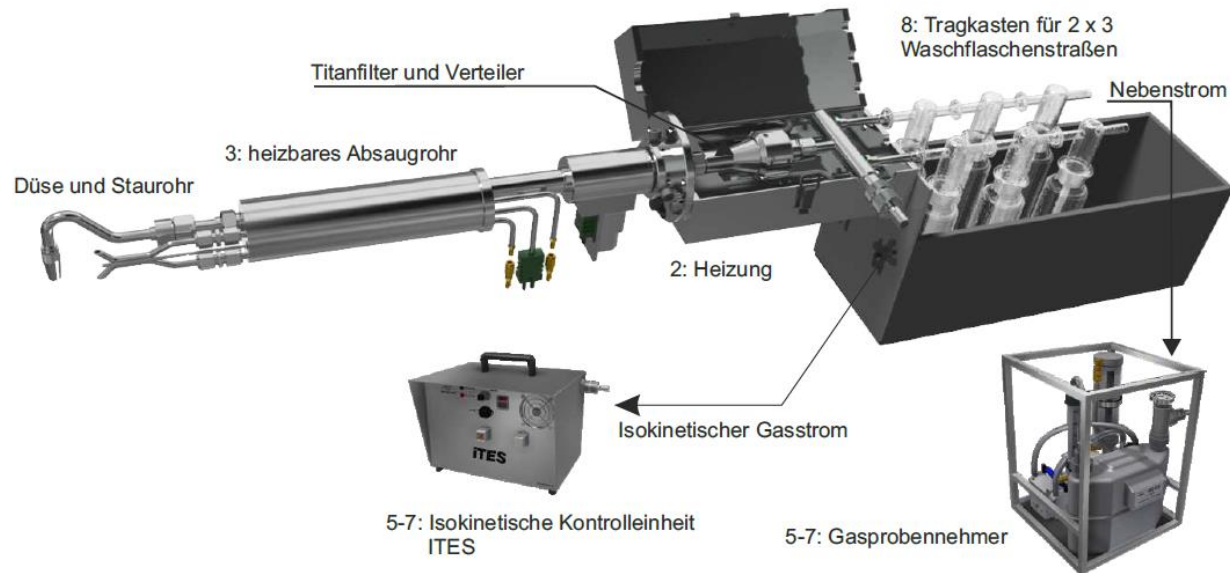
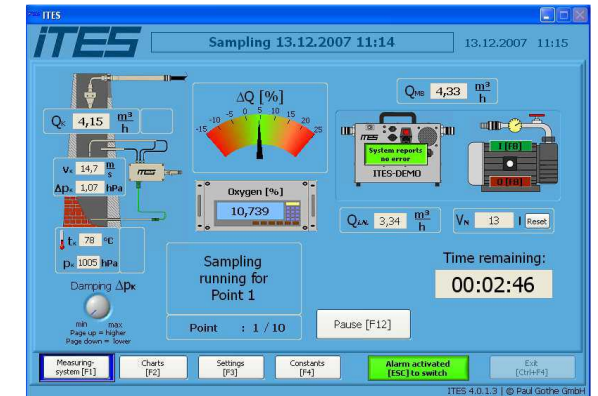
Non extractive

Across the slag pit

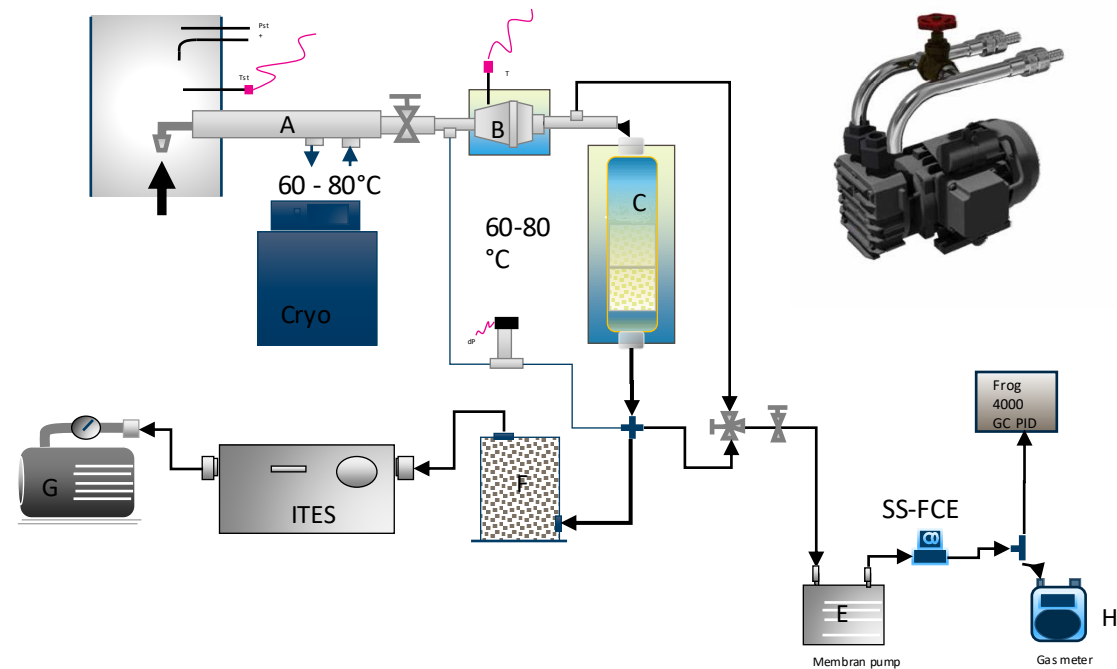
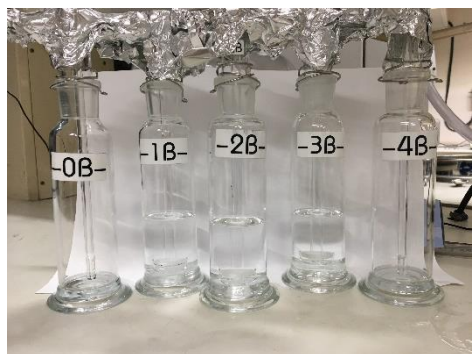
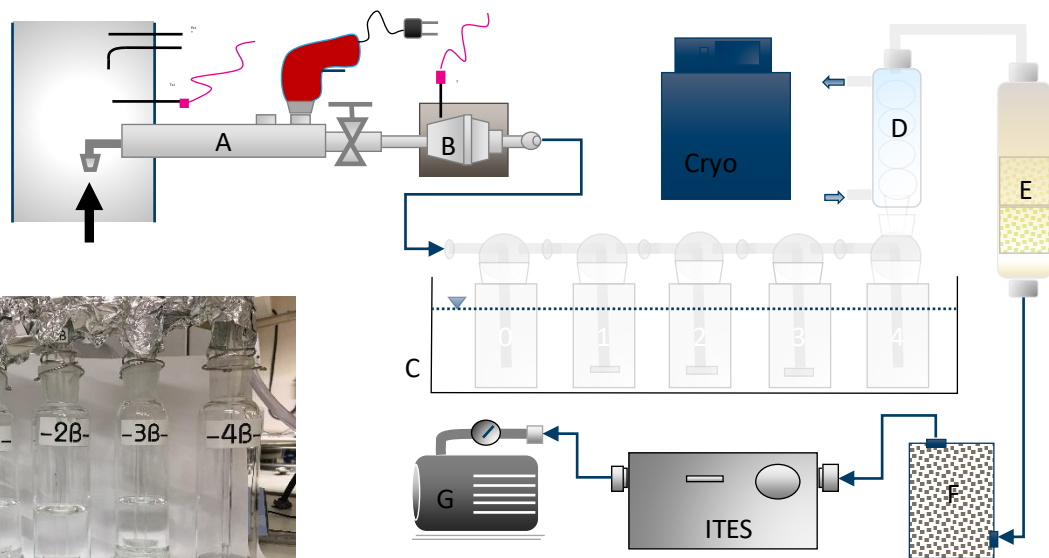
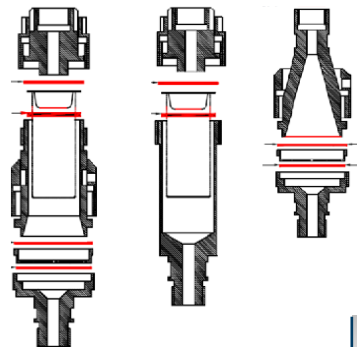


ITES Automatic isokinetic sampler

Sample flow rate 0.4 to 4 m³/h

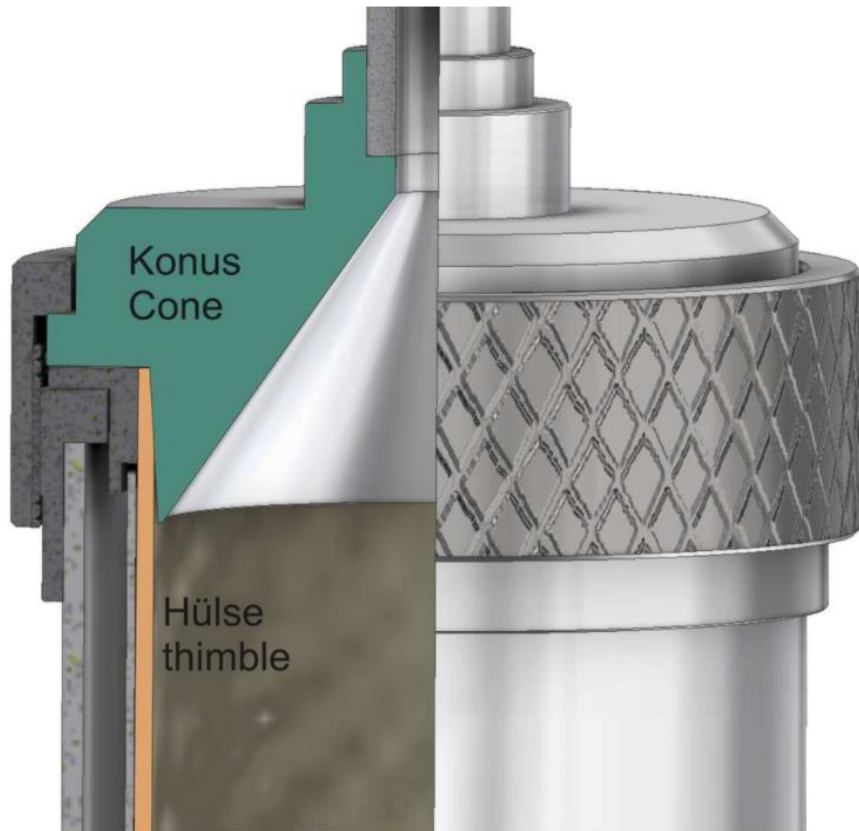


Toolbox



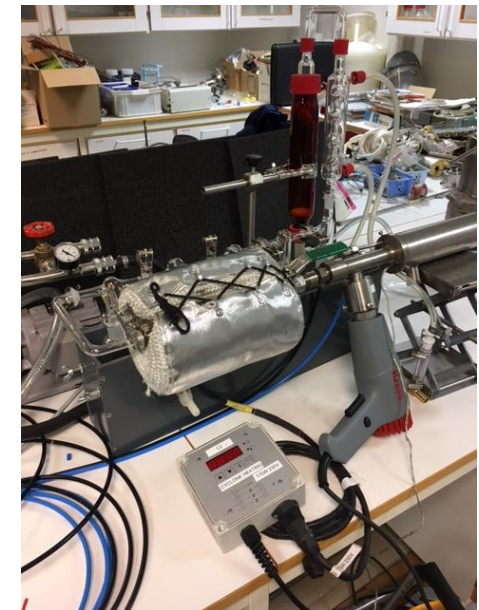
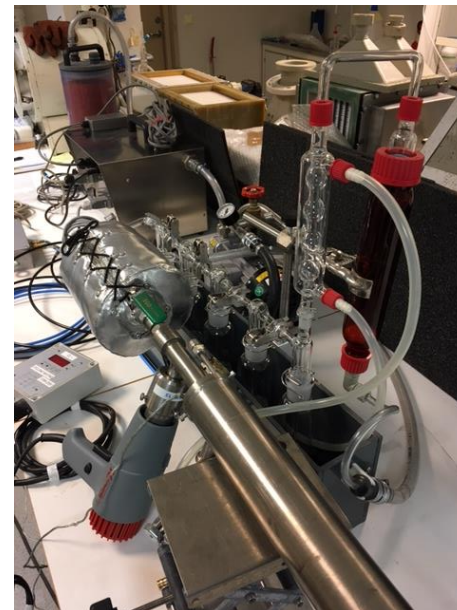
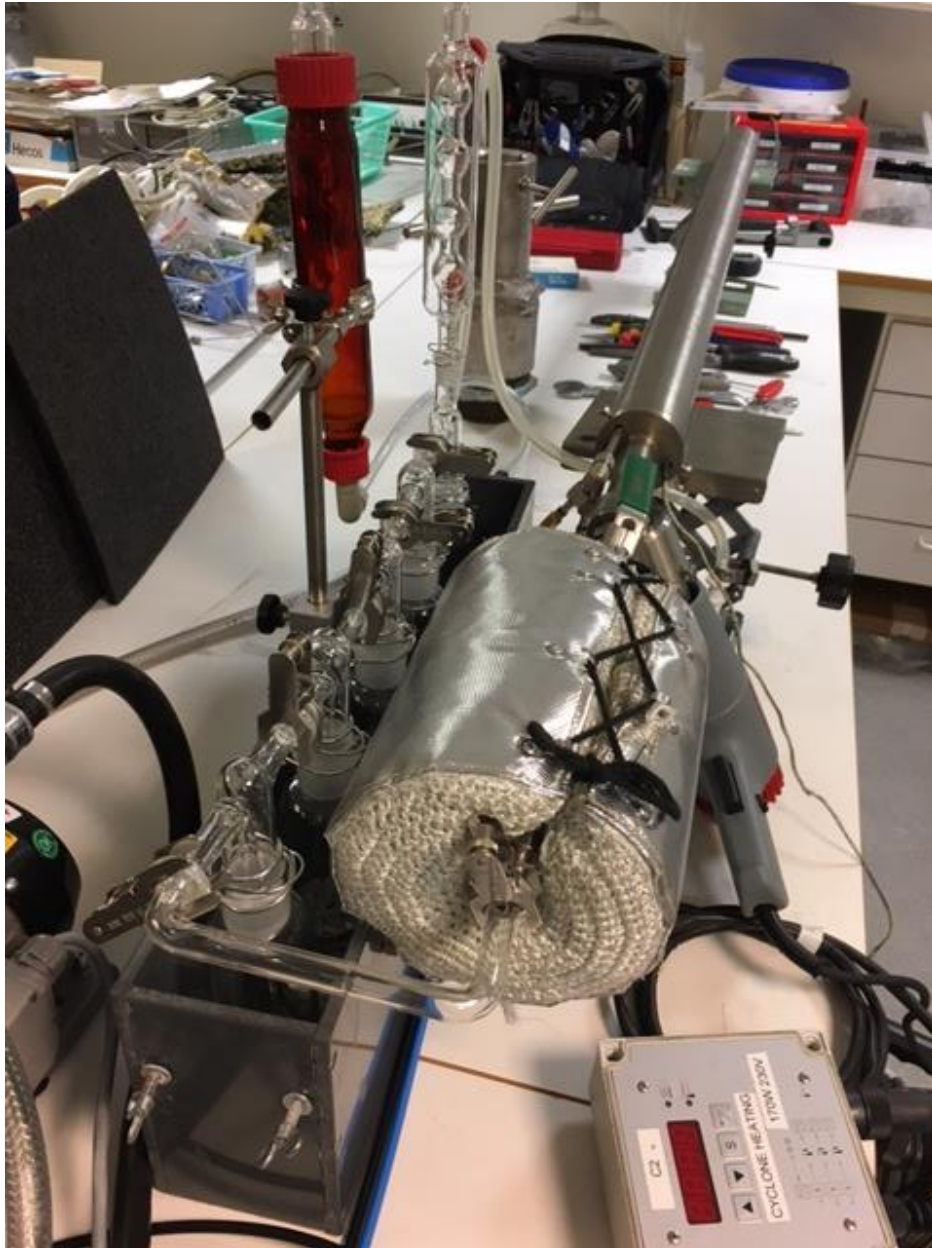
TF Filter

https://www.paulgothe.com/epages/62307369.sf/en_GB/?ObjectPath=/Shops/62307369/Products/13.05



Filter size $\varnothing$ 56 mm, length 150 mm





Analysis Equipment

Combustion gas, VOC and TOC analysers

Type C : Gas Chromatography,
with different types of columns and detectors

H₂, O₂, N₂, CO, CO₂, CH₄, COS, Ethene
Ethane, VOC, Naphthalene

Principle:

A mixture of different gas molecules is passed through a narrow capillary. Depended on their structure the compounds interact differently with the surface of the stationary phase inside the column and elute at a different time.

A suited detector monitors the changes of a specific response relative to the injection time.

Retention time together detector response (signal strengths) can be attributed to the concentration of a specific compound (calibration)

Typical types

TC Detector: Change in thermal conductivity

FI Detector: Flame ionization



Analysis Equipment > C6-C12 analyser

Compound concentration **vs** Background

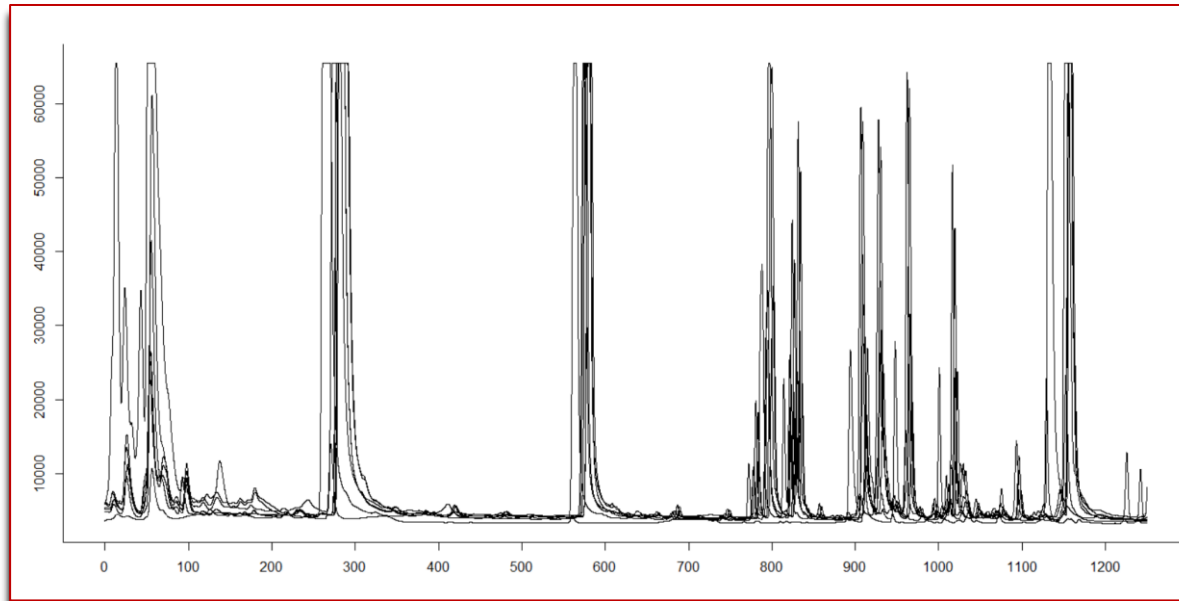
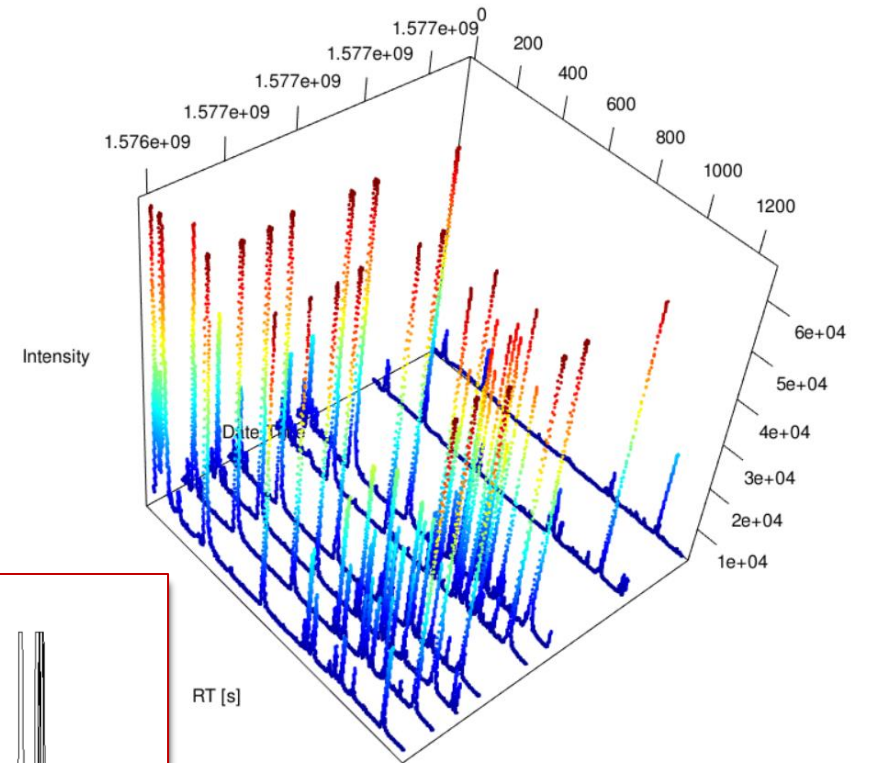
- Filtration / condensate removal

Molecular weight/aggregate state **vs** Analysis method

- Gas phase only

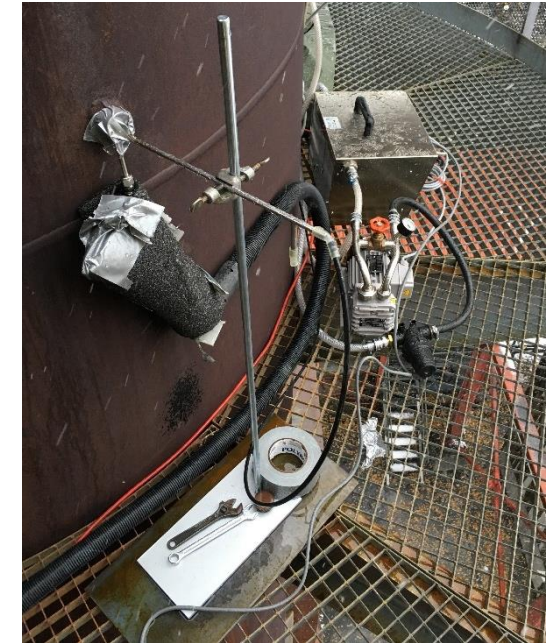
Time resolution **vs** sensitivity

- Relatively fast analysis (80 sec – 30 min)
- XX ppm - MicroGC TDC
- ppt level – AirmoVoc (BETX - concentration trap, FID)



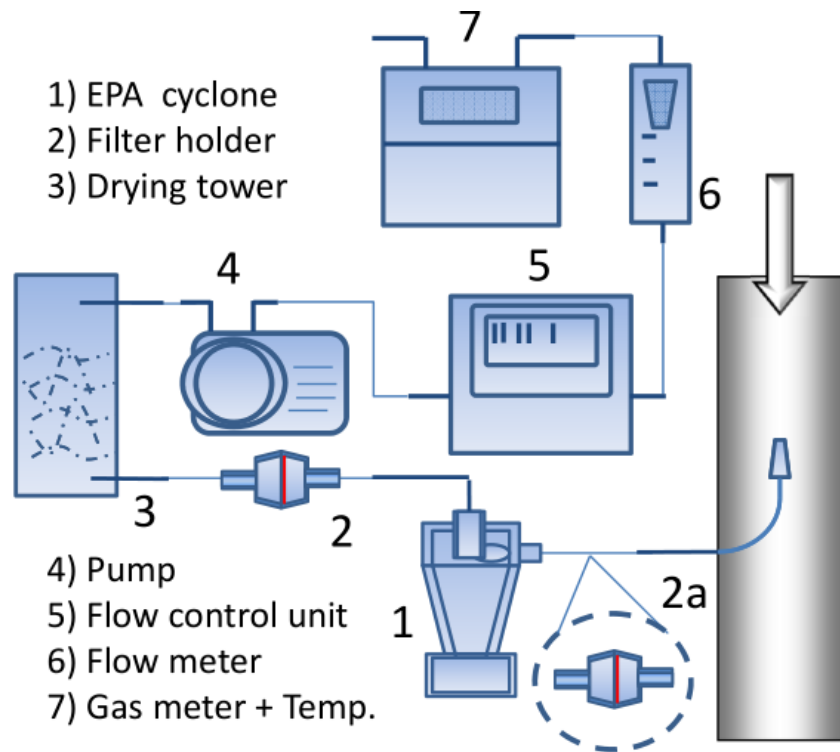
PAH Sampling

ELKEM Thamshavn



Example: Dust composition vs particle size

ISOK4 : TPS4 Experimental setup

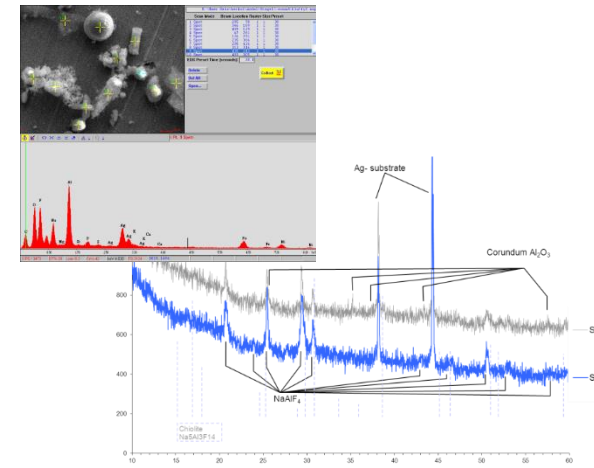


Sampling of process gases under different operational conditions as varying temperature and volumetric flow. (Filter resistance)

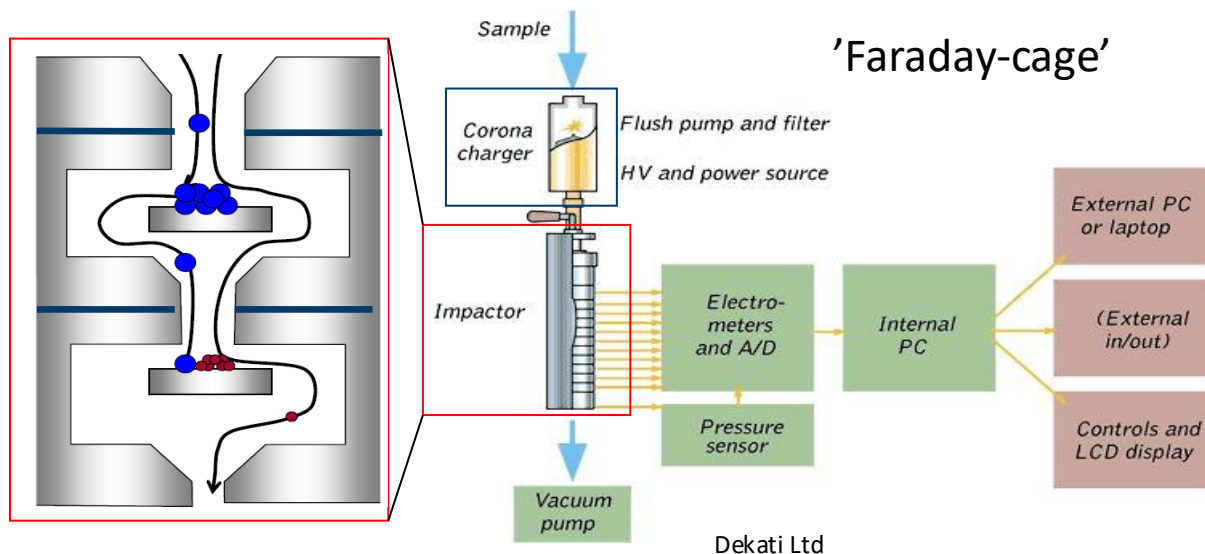


Impactor ELPI (Dekati)

- Coarse fraction
 - Captured in standard EPA-cyclone + 10 μm
- Cascade impactor samples
 - $7\text{ nm} < D_i < 10\text{ }\mu\text{m}$

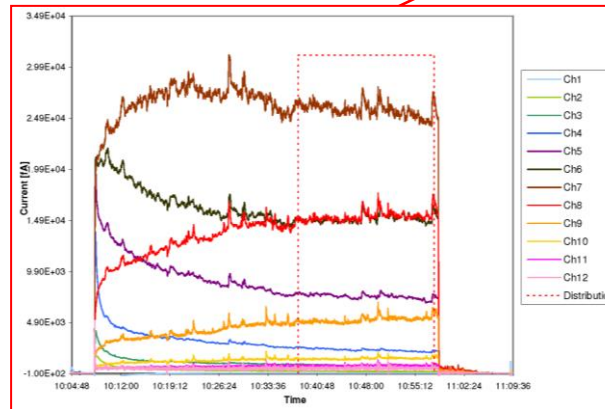
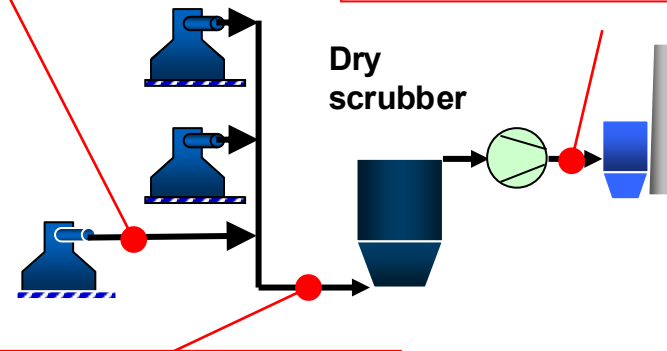
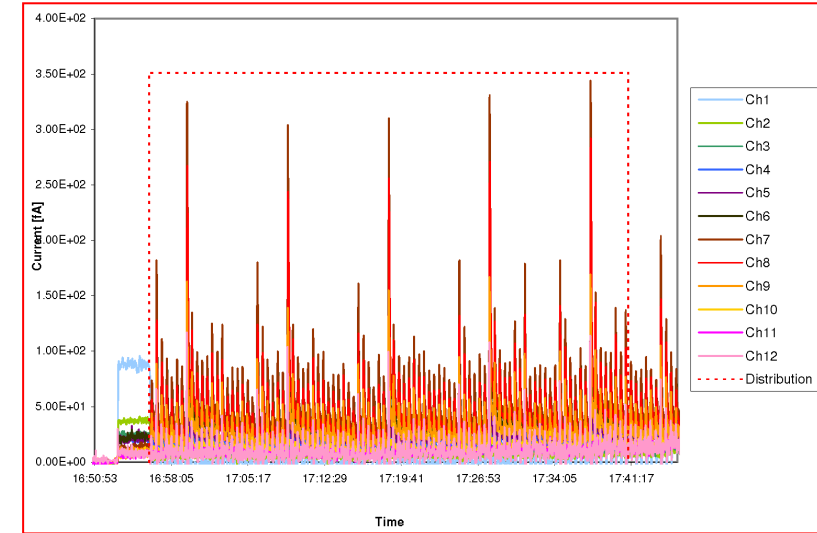
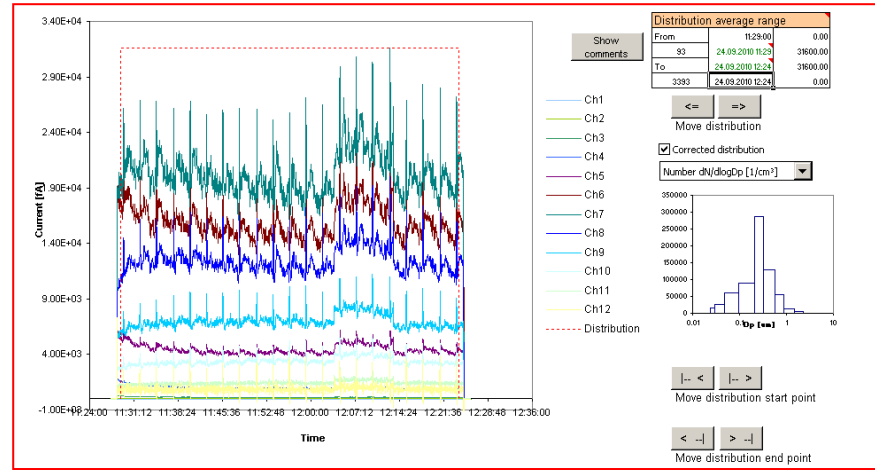


XRD, XPS
SEM, EDS
ICP-MS



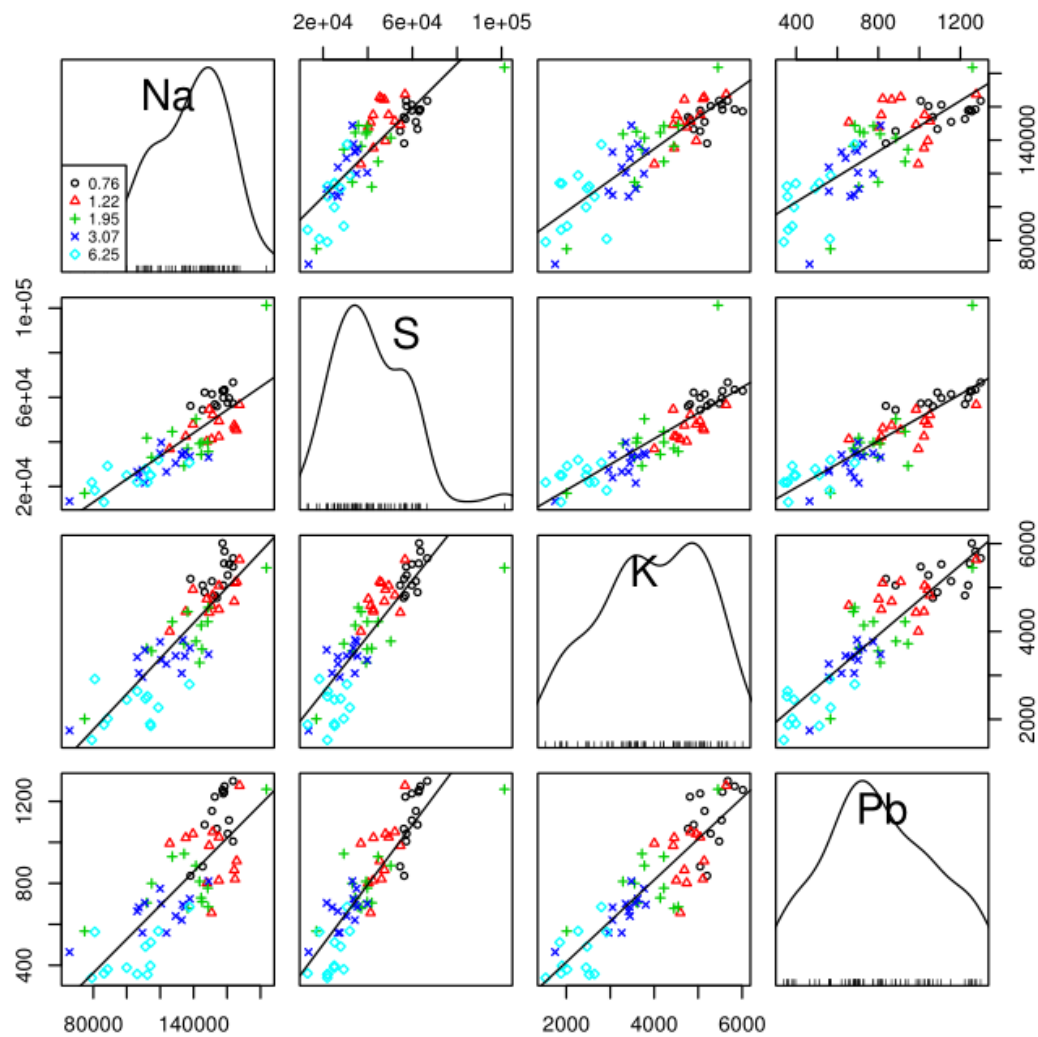
Sampling

- Hall-Héroult process



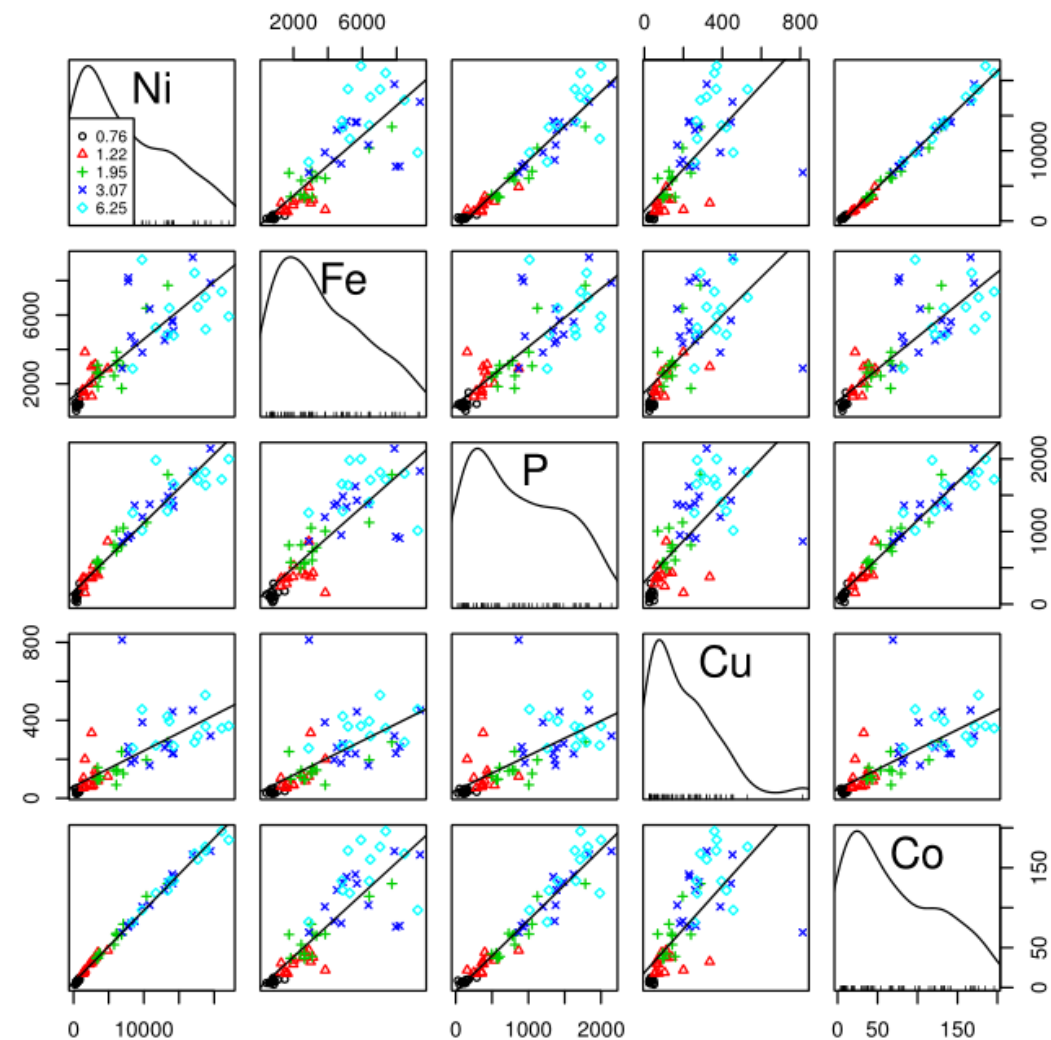
ELPI

Particle size distribution –
Trace element concentration



μm

- 0.76
- △ 1.22
- + 1.95
- × 3.07
- ◇ 6.25

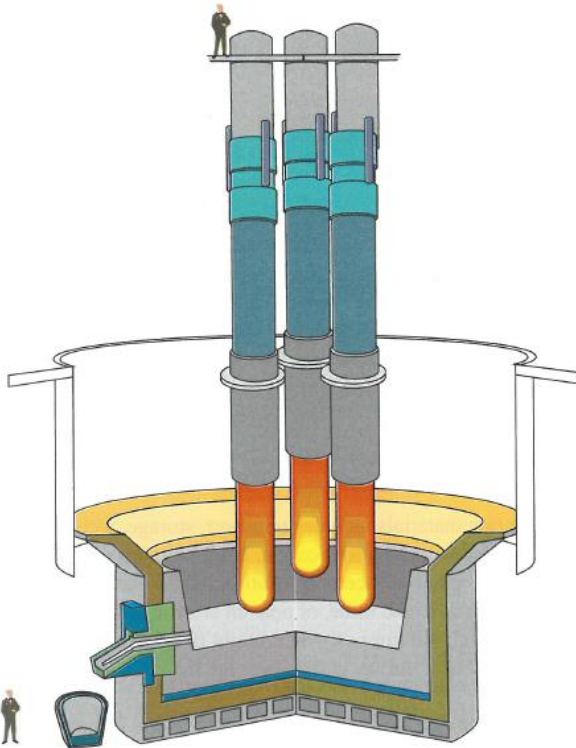


Carbothermic reduction of oxides to metal

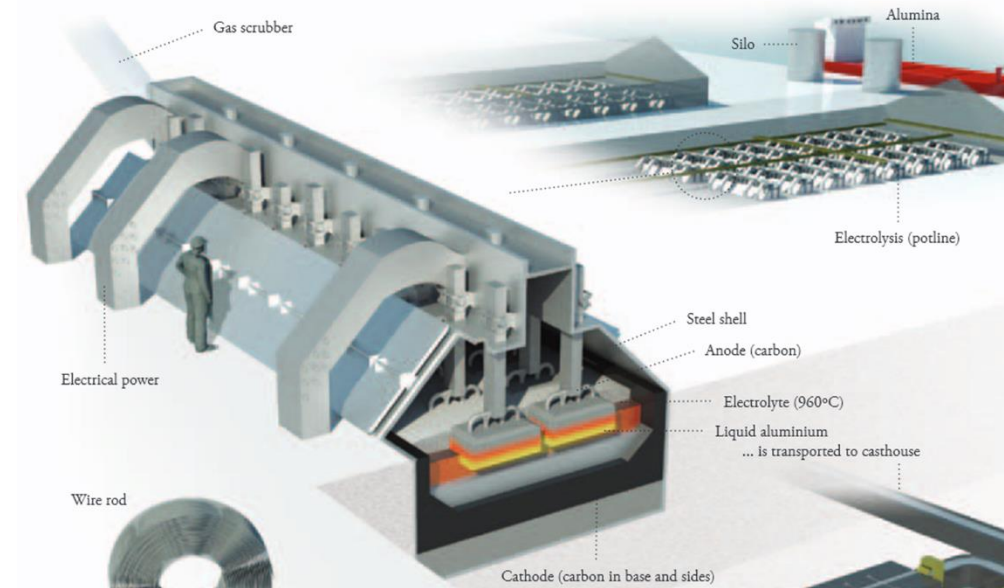
Aluminium and Ferroalloy industry

Ferroalloy industry (FeSi, FeMn, SiMn) or related industries (Si, Fe and TiO_2)

- typically, in electric arc furnaces by passing electric current through carbon based electrodes, charge material and melt.



Aluminium smelting process

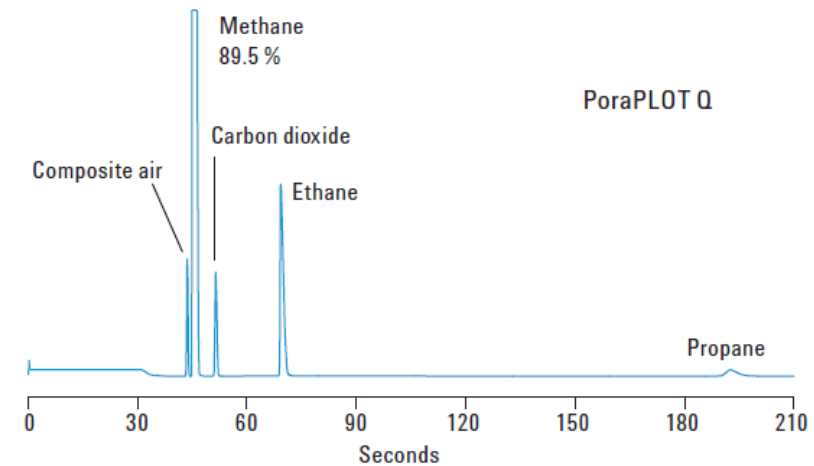
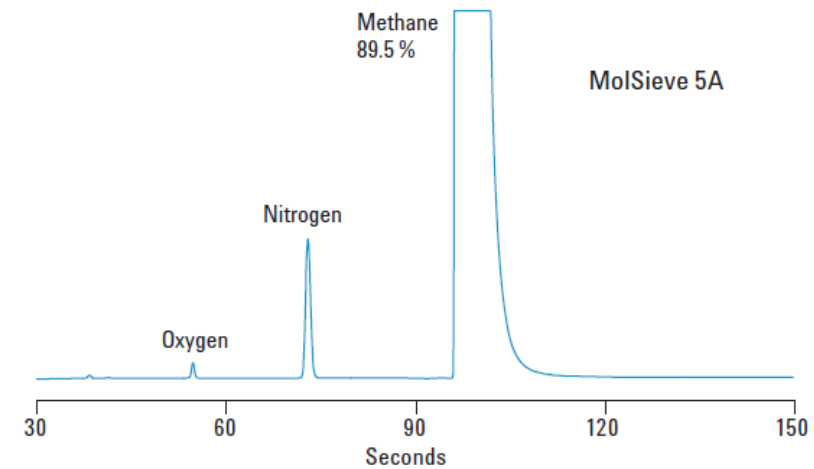


© hydro.com:
Aluminium_environment-and-society

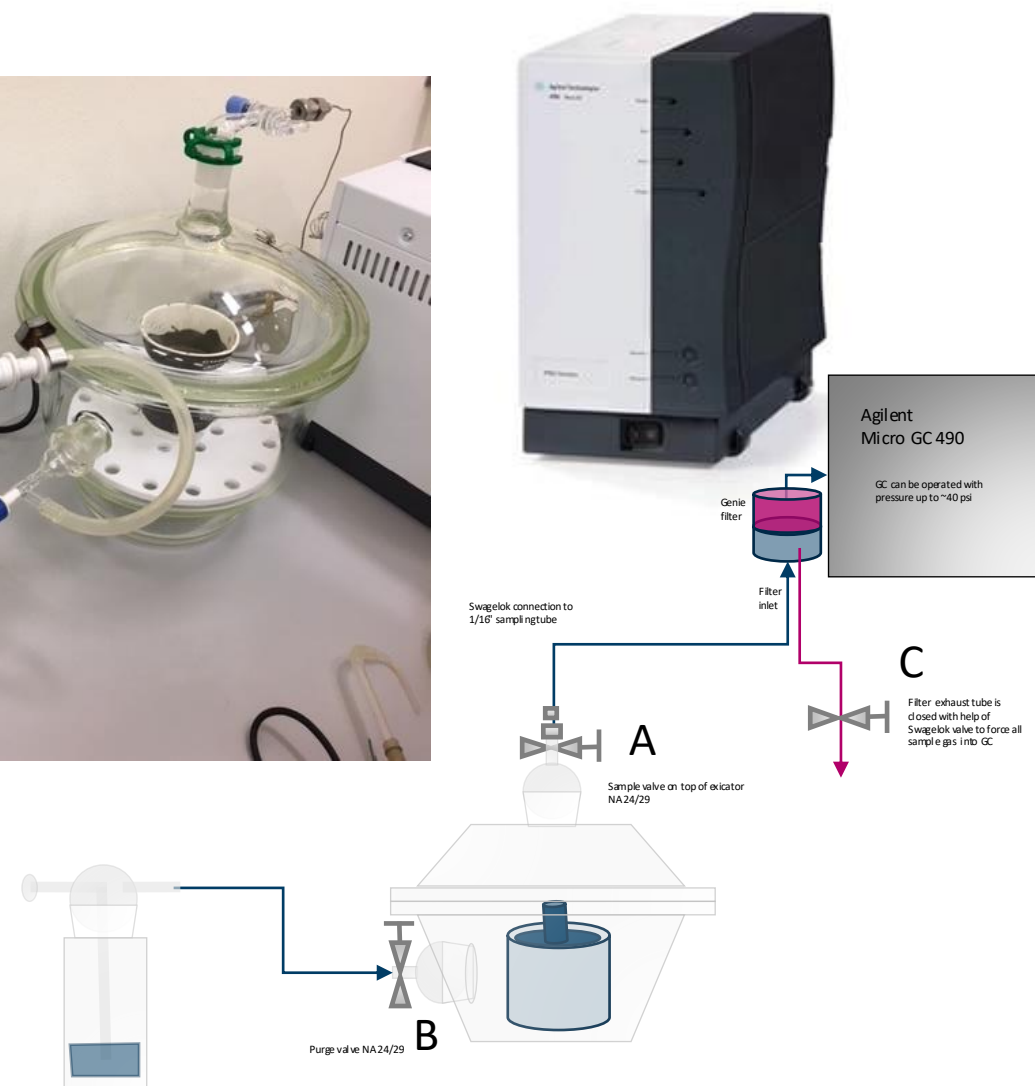
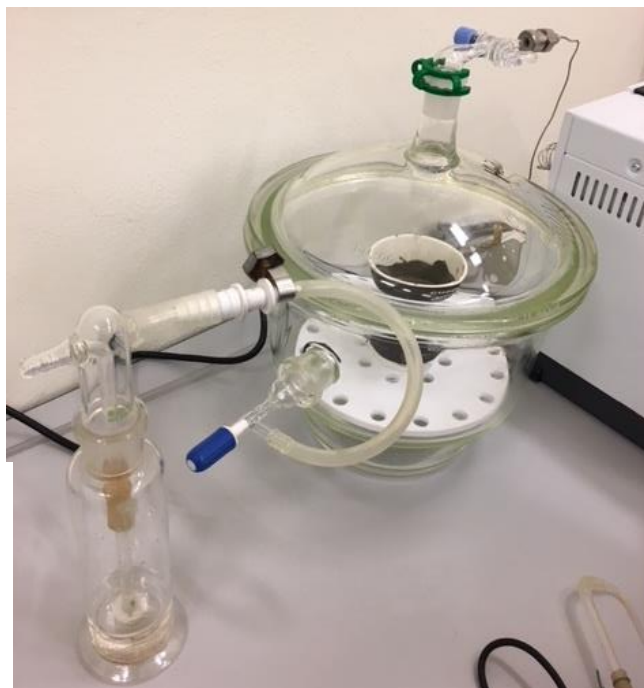
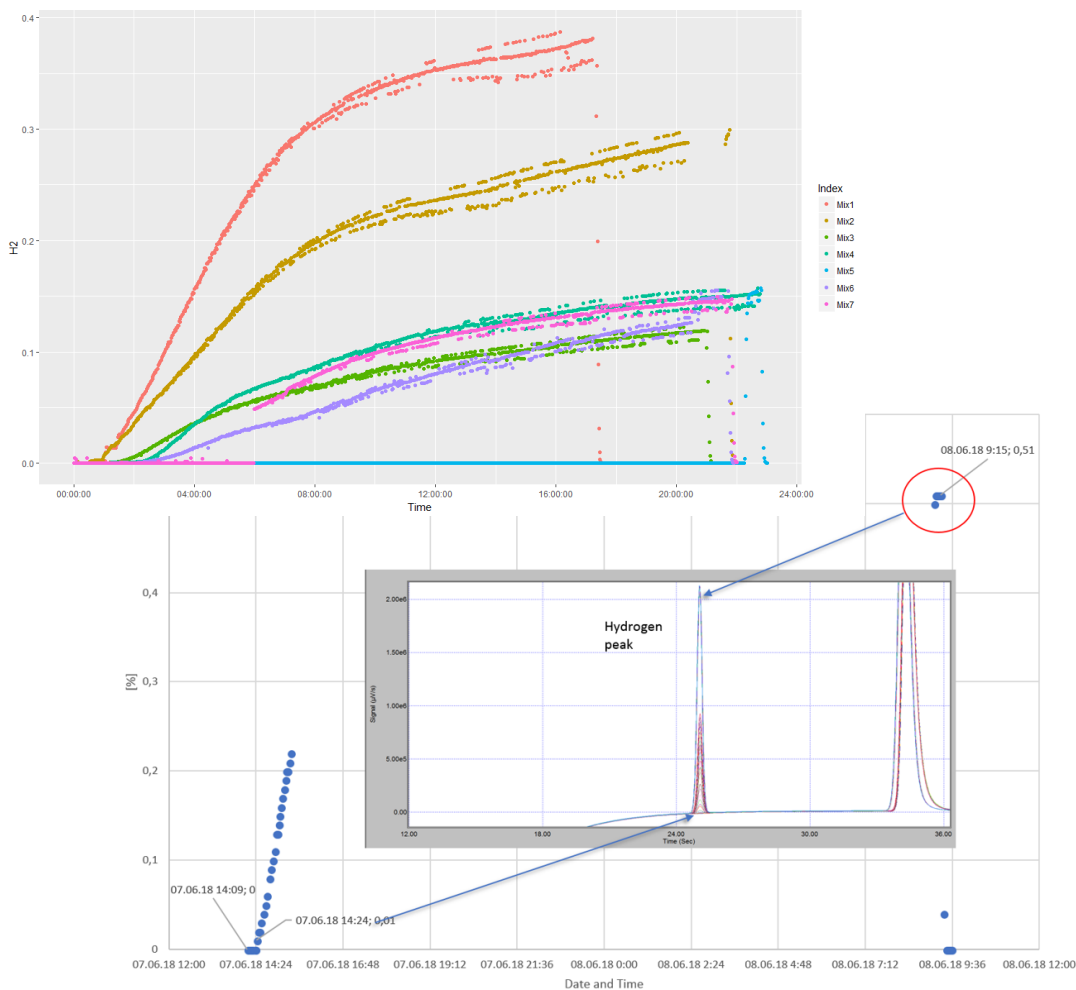
Agilent 490 Micro GC



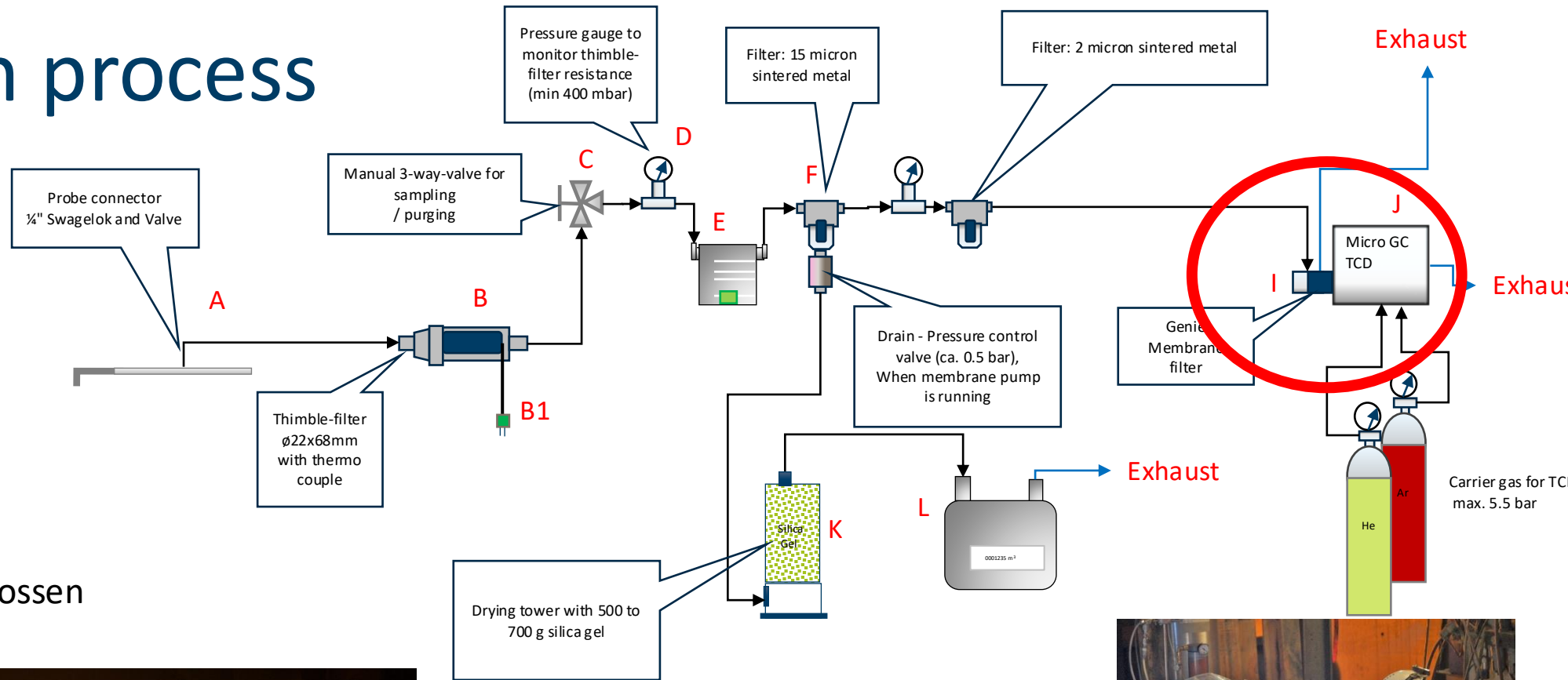
"Portable" Gas Chromatograph



Micro GC - H₂ evolution: Al reinforced concrete



Micro GC in process metallurgy



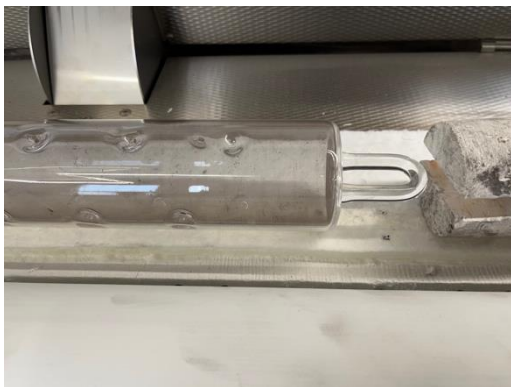
ELKEM Bjølvfossen



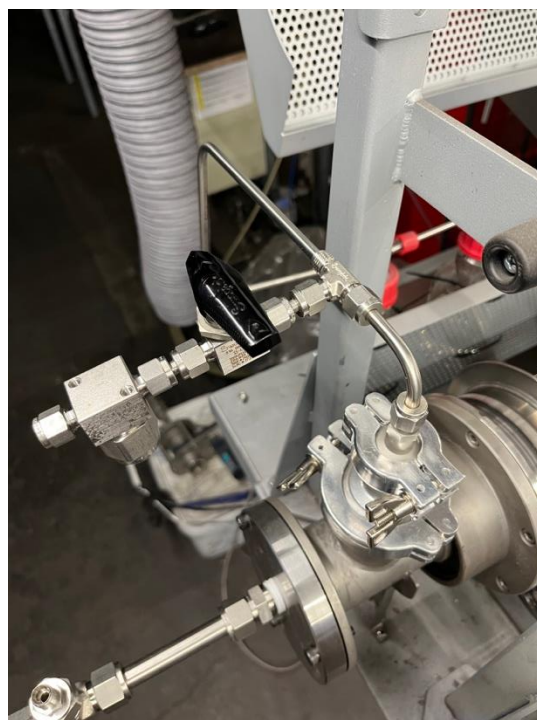
Lille Trille



Reaction chamber insert



H₂ Gas inlet (with thermocouple)
Outlet with bleed to GC (15μm filter)

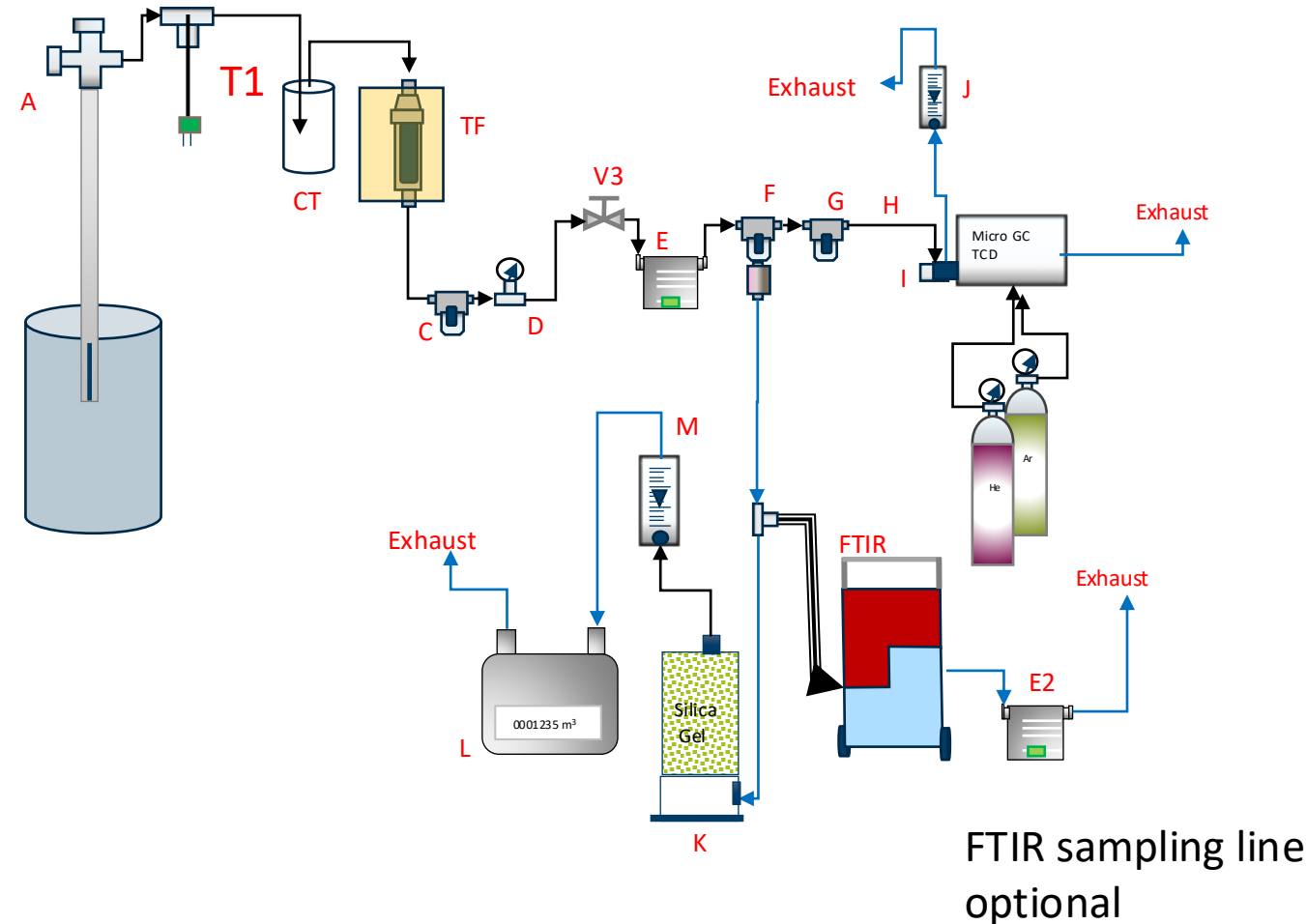


N₂ or Ar purge

RAW-GAS SAMPLING



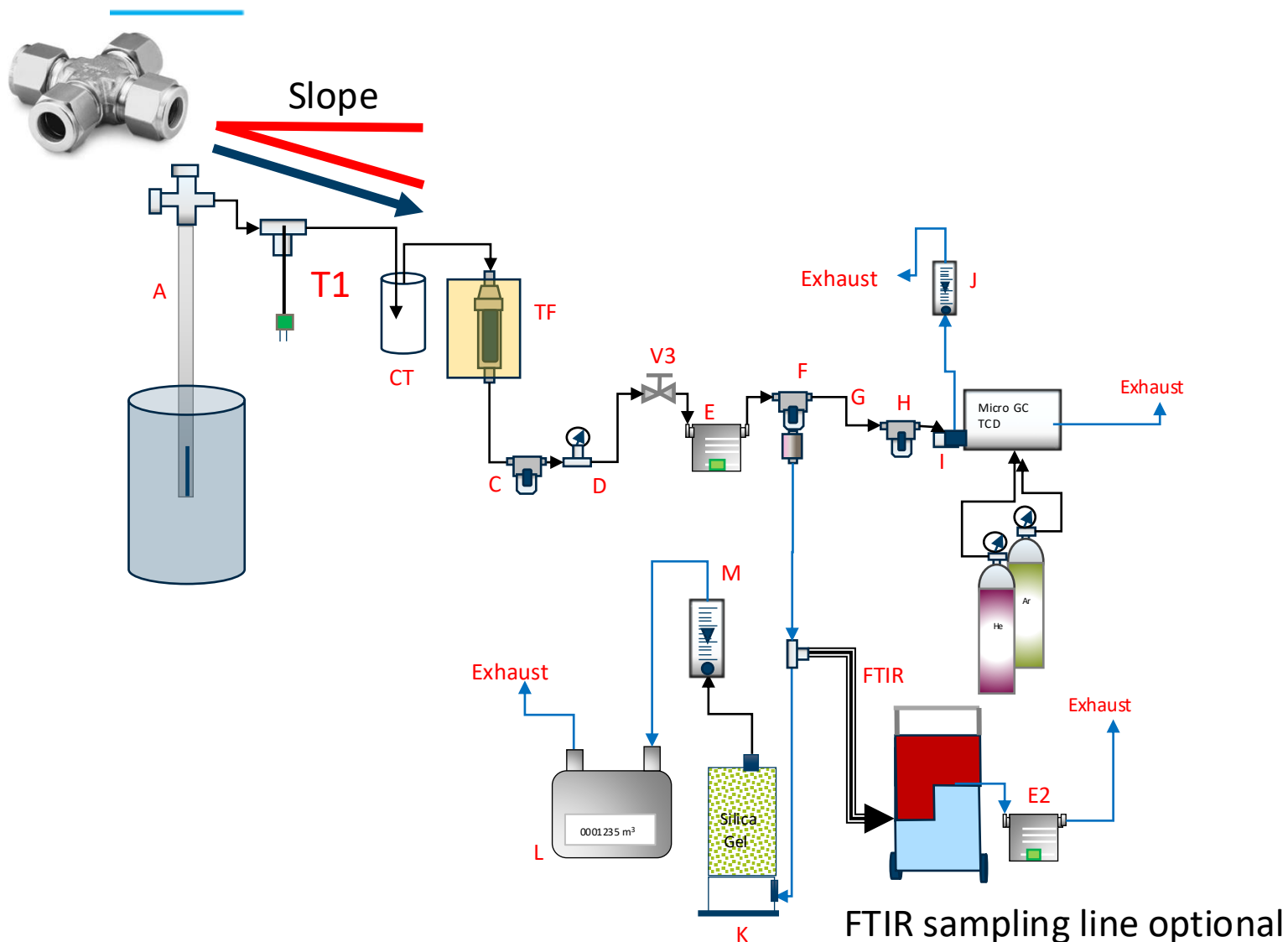
Raw-gas Sampling-line: GC-ProtIR 204M setup



Components

- A) Slotted probe: ½" Swagelok tube connector
- T1) Thermocouple in t-union ½" connected to probe with PFA tubing
- V1) Swagelok Ball valve ½" tube connector
- CT) Condensate trap (gas tight stainless steel vessel, 1.5 l volume)
- TF) Thimble Filter (+ heating jacketed)
- C) Swagelok Filter (¼" tubing) 60µm sintered metal
- D) Pressure gauge LEO-Record Gauge/temperature
- E) Membrane pump
- V3) Needle Valve to control flow with help of rotameter/ (M)
- Gas meter (L)
- Silica gel Drying Tower (K)

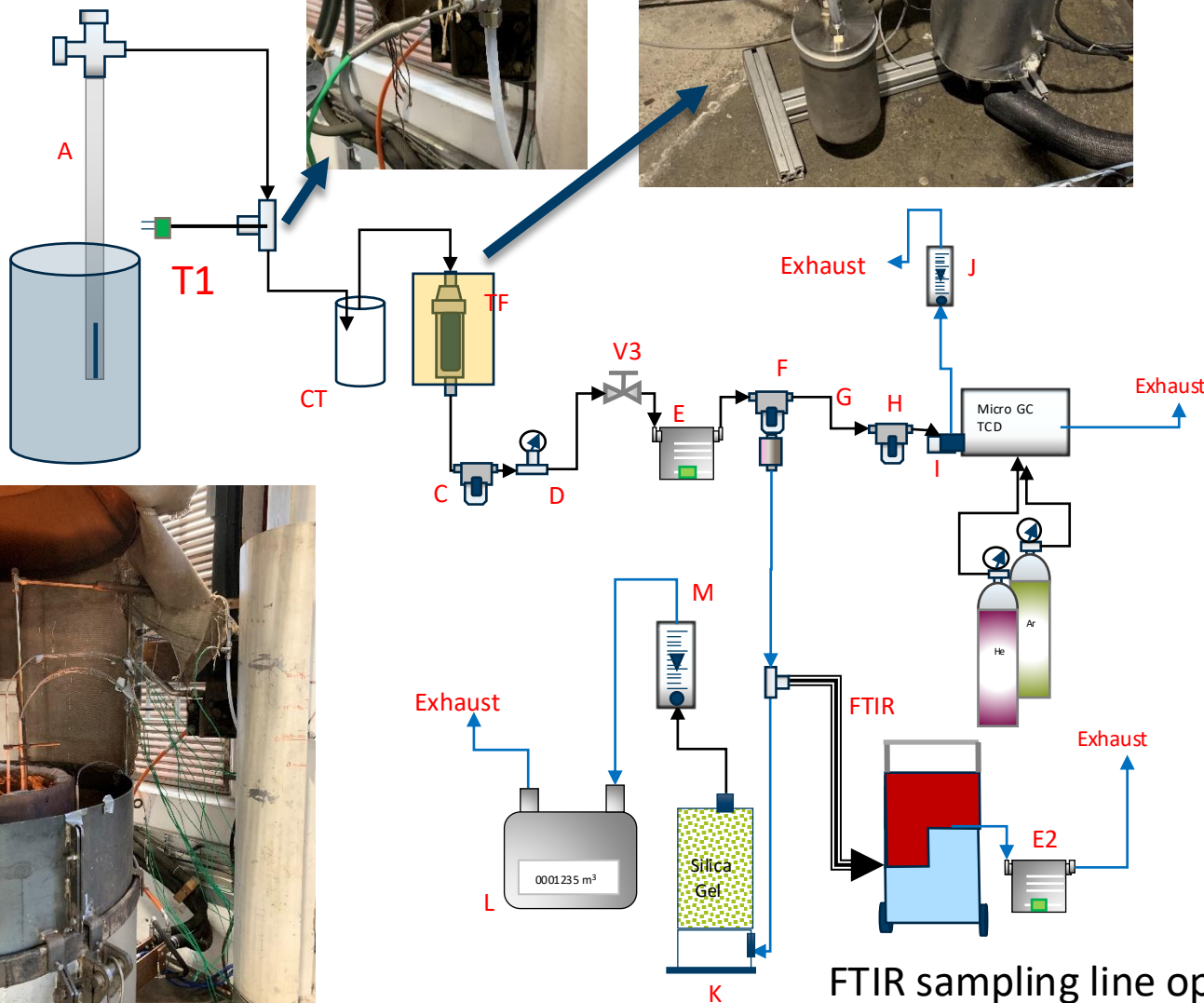
Raw-gas Sampling-line: GC-ProtIR 204M setup



Components

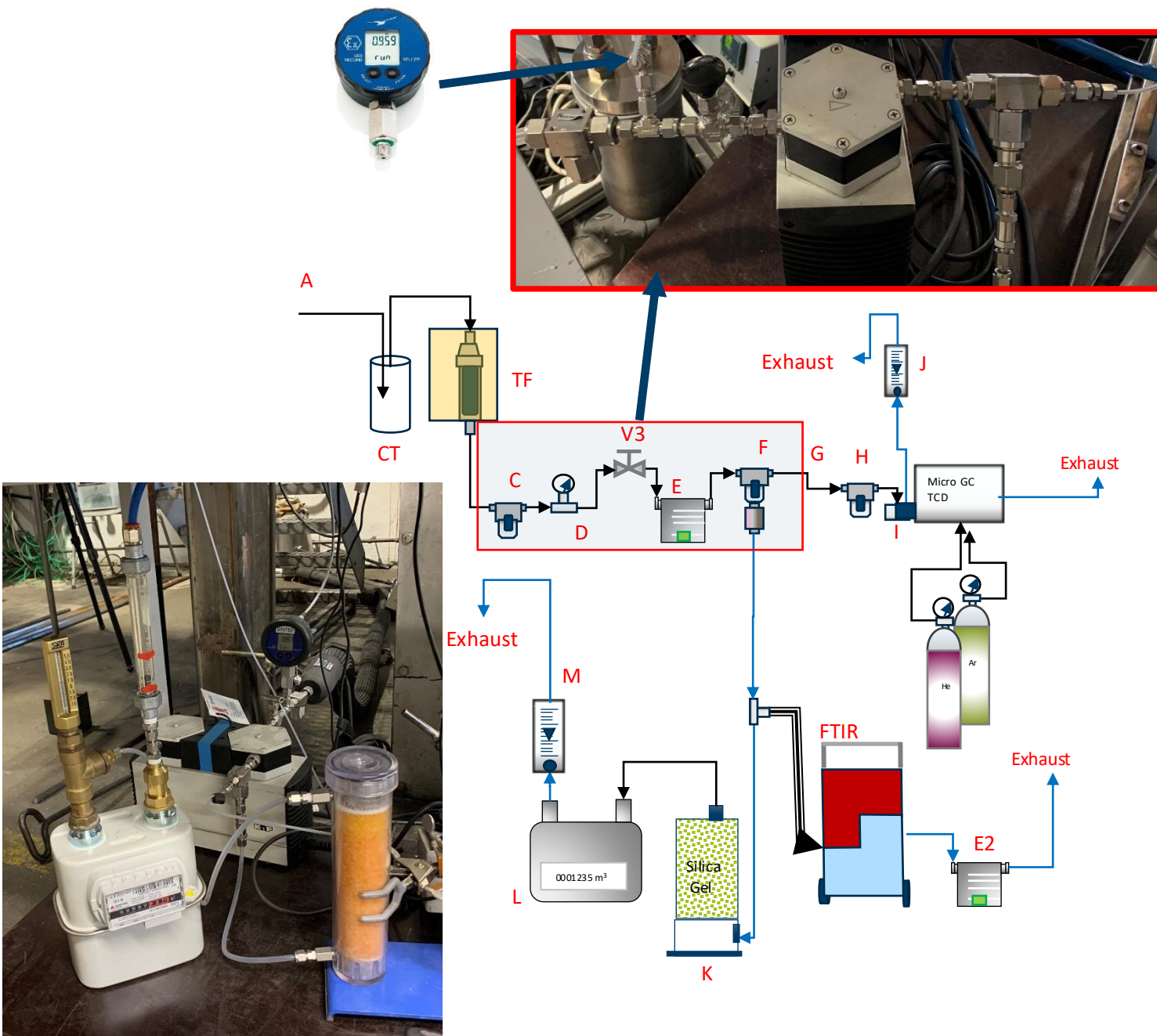
- A) Slotted probe: ½" Swagelok tube connector, with Swagelok tube fittings (Union-Cross 1/2" and caps)
- T1) Thermocouple in t-union ½" connected to probe with PFA tubing
- Tubing from slotted probe to condensation trap CT must be sloped to make sure that condensates are drained away from furnace (HSE!)
Condense trap (gas tight stainless steel vessel, ca 1.5 l volume)

Setup



Components

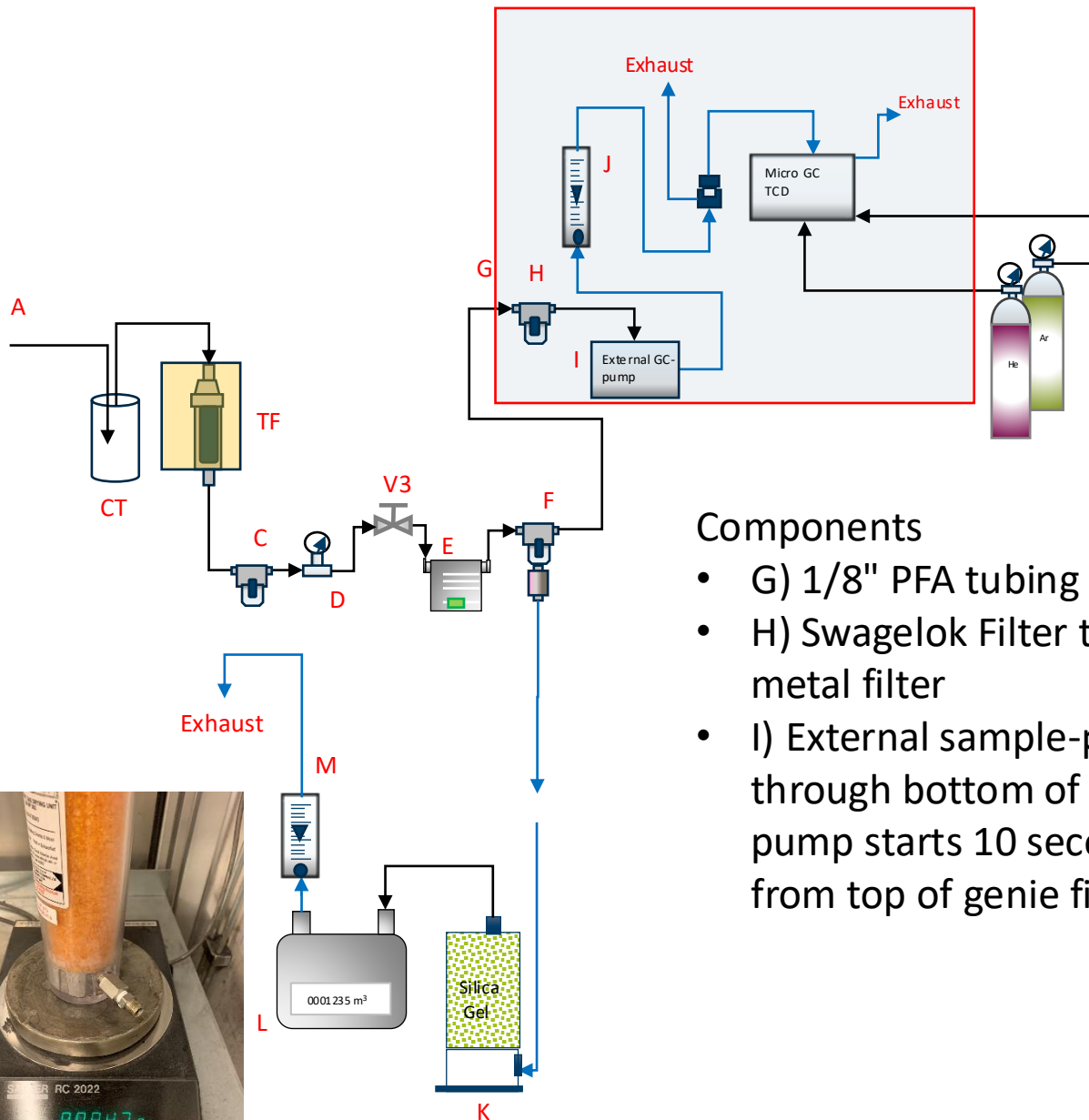
- T1) Thermocouple in t-union ½" connected to probe with PFA tubing (electrically insulated from probe)
- TF) Thimble Filter (+ heating jacketed)
- C) Swagelok Filter (¼" tubing) 60µm sintered metal
- D) Pressure gauge LEO-Record Gauge/temperature
- E) Membrane pump
- V3) Needle Valve to control flow with help of rotameter/ (M)
- Gas meter (L)
- Silica gel Drying Tower (K)



Components

- C) Swagelok Filter (1/4" tubing) 60μm sintered metal
- D) Pressure gauge LEO-Record Gauge/temperature
- E) Membrane pump
- F) Swagelok filter med bypass port and check-valve 1/3 psi
- V3) Needle Valve to control flow with help of rotameter/ (M)
- Gas meter (L)
- Silica gel Drying Tower (K)



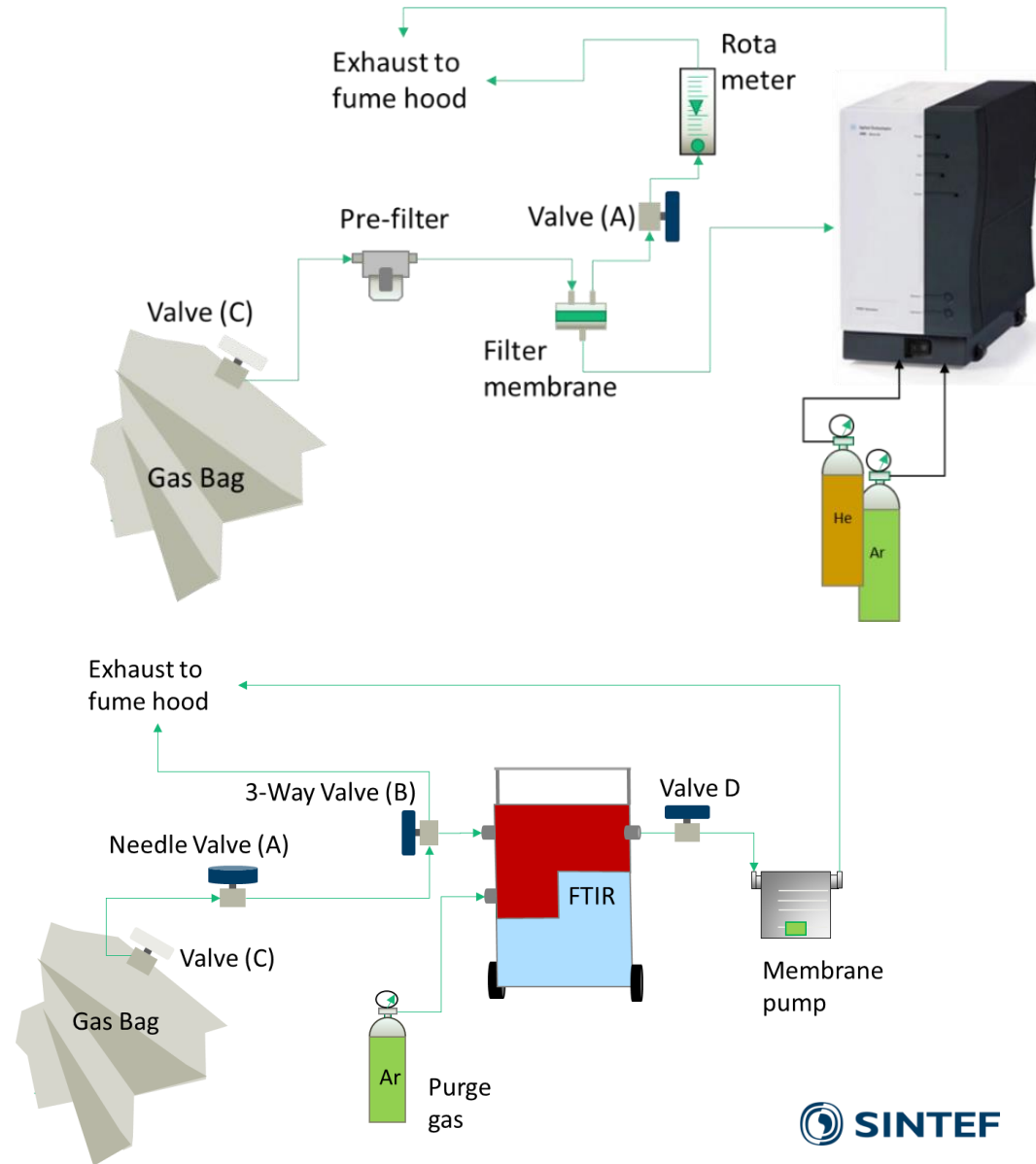
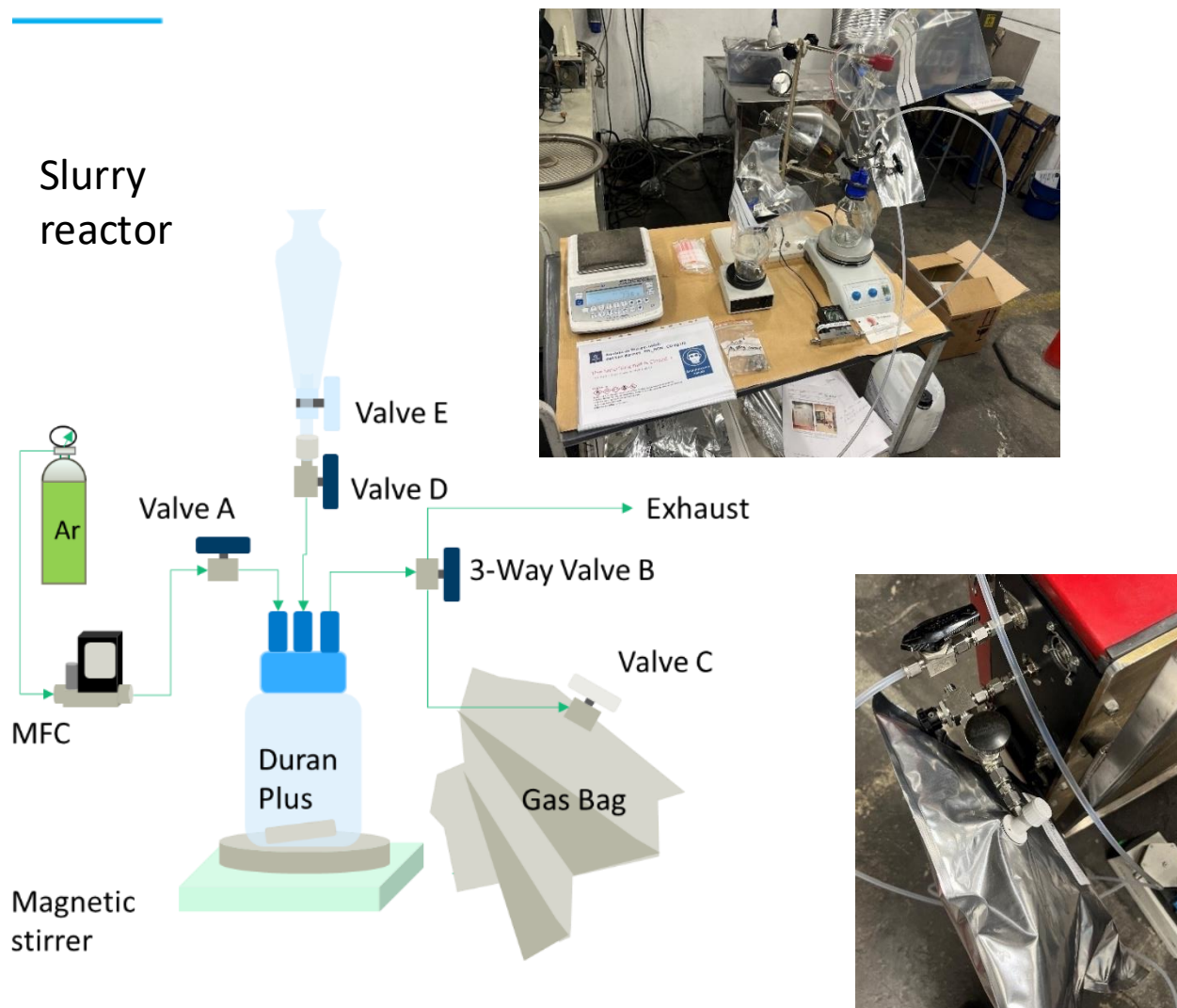


Components

- G) 1/8" PFA tubing between Filter F og Filter H
- H) Swagelok Filter type TF with 2 μ m sintered metal filter
- I) External sample-pump (flow rate 50 ml/min through bottom of Genie filter) – external pump starts 10 seconds before GC samples from top of genie filer

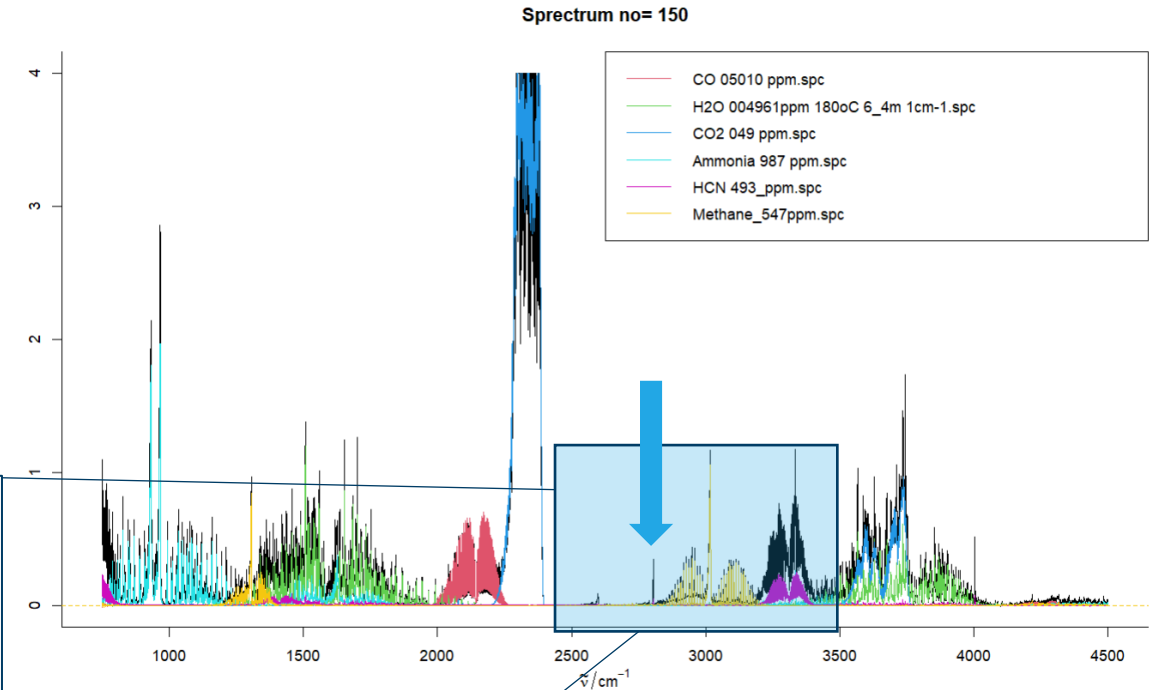
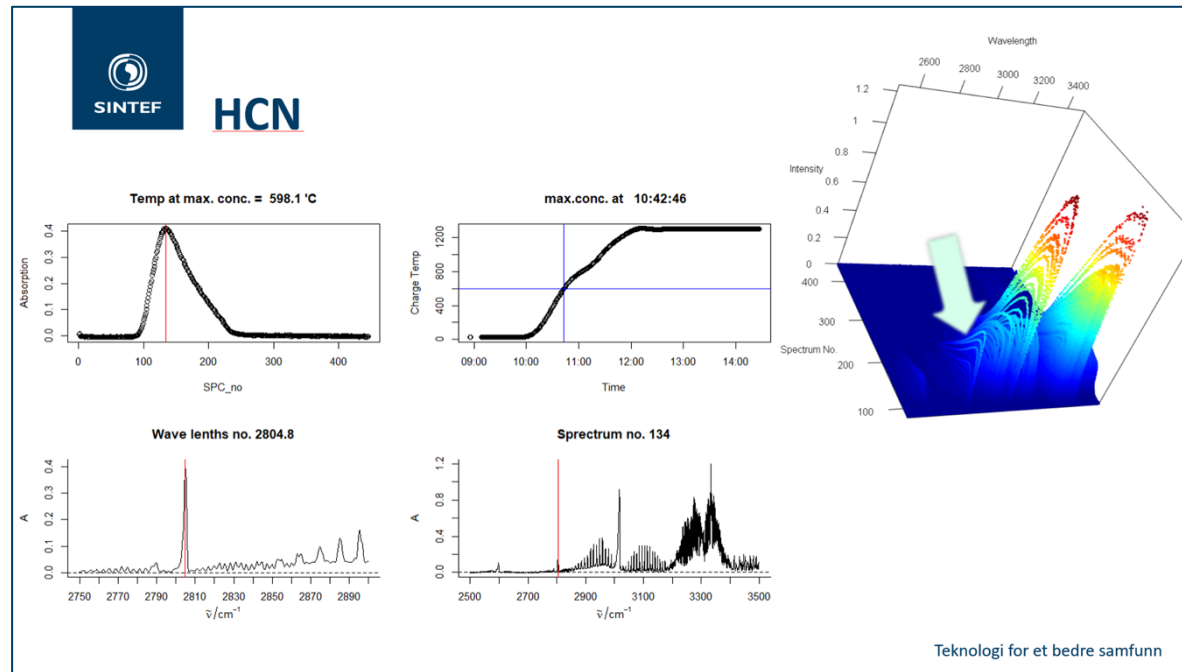


PH3 HCN analysis (Gasbag)



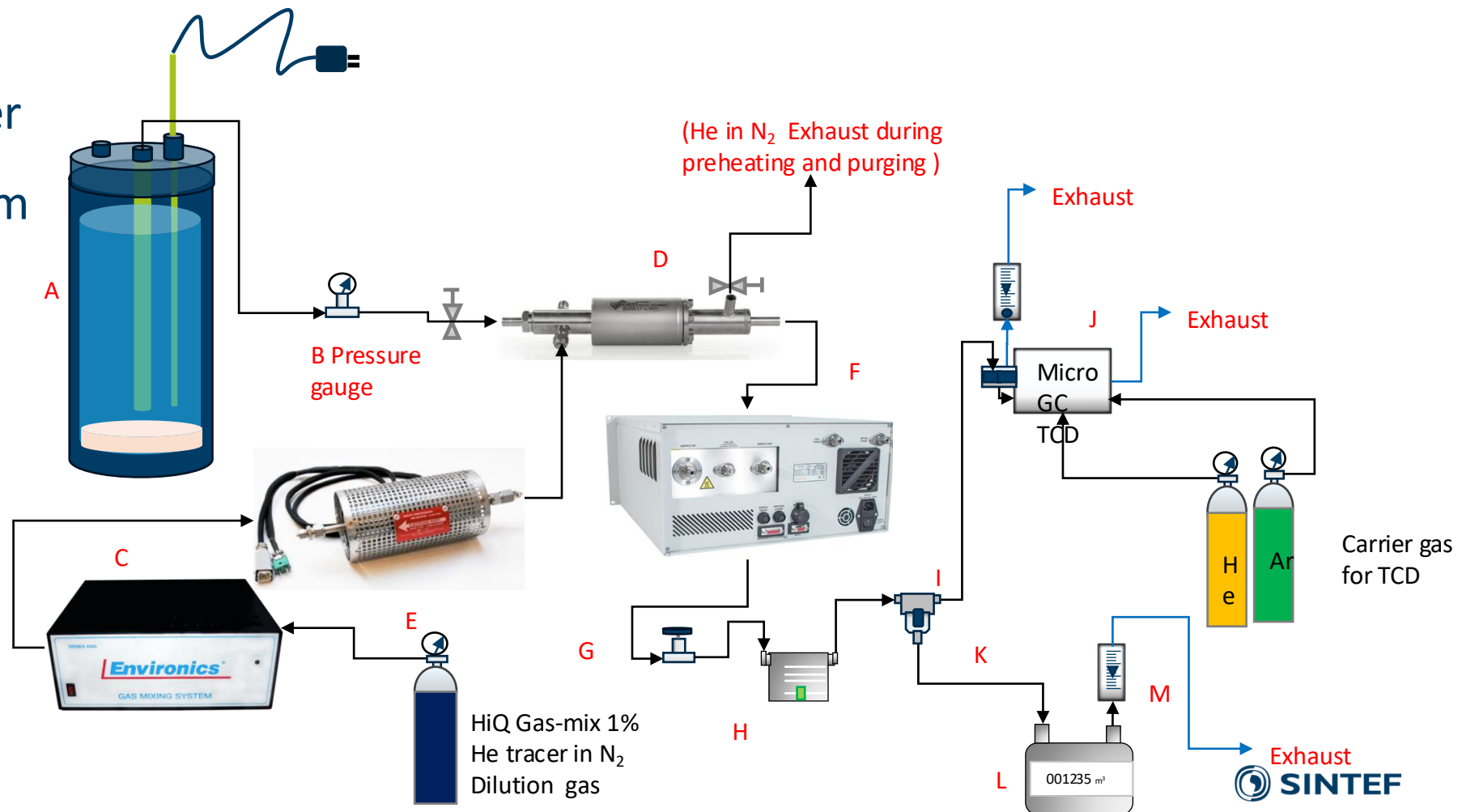
HCN analysis

- HCN in off gas

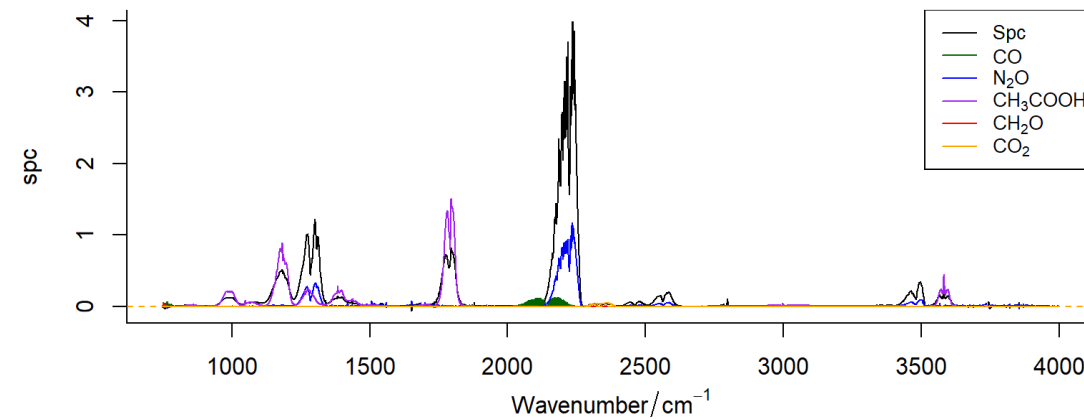


NO_x – high concentration setup

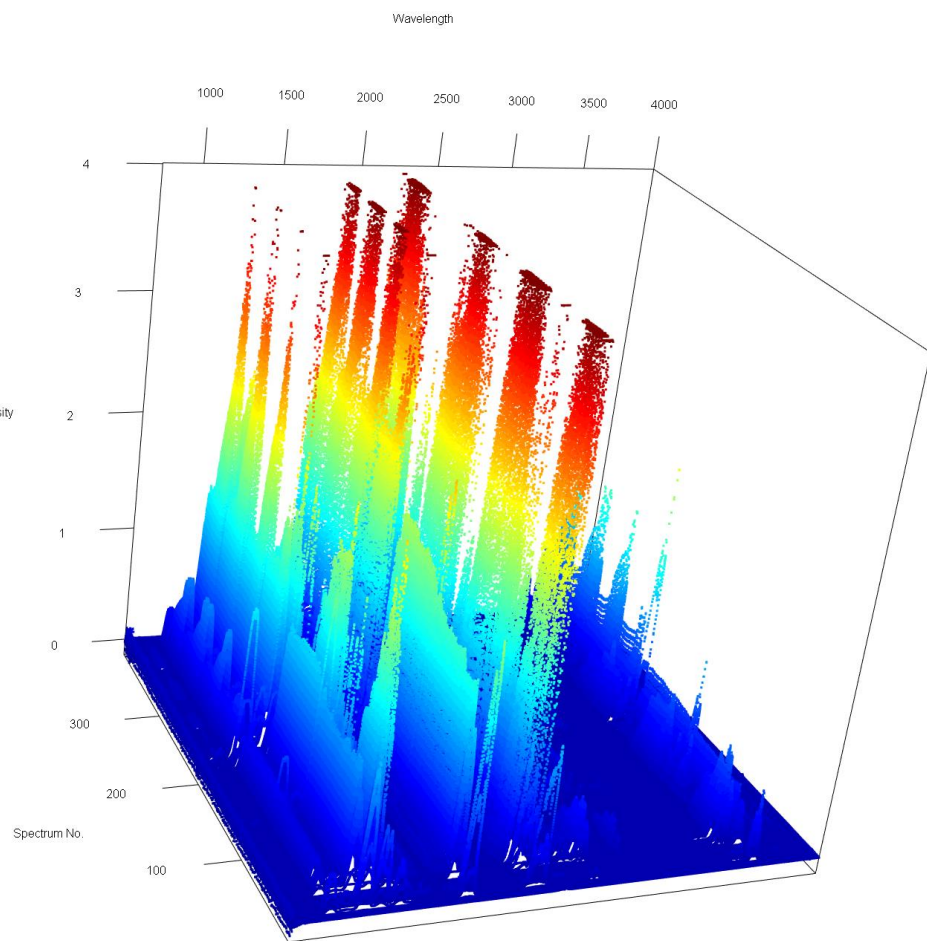
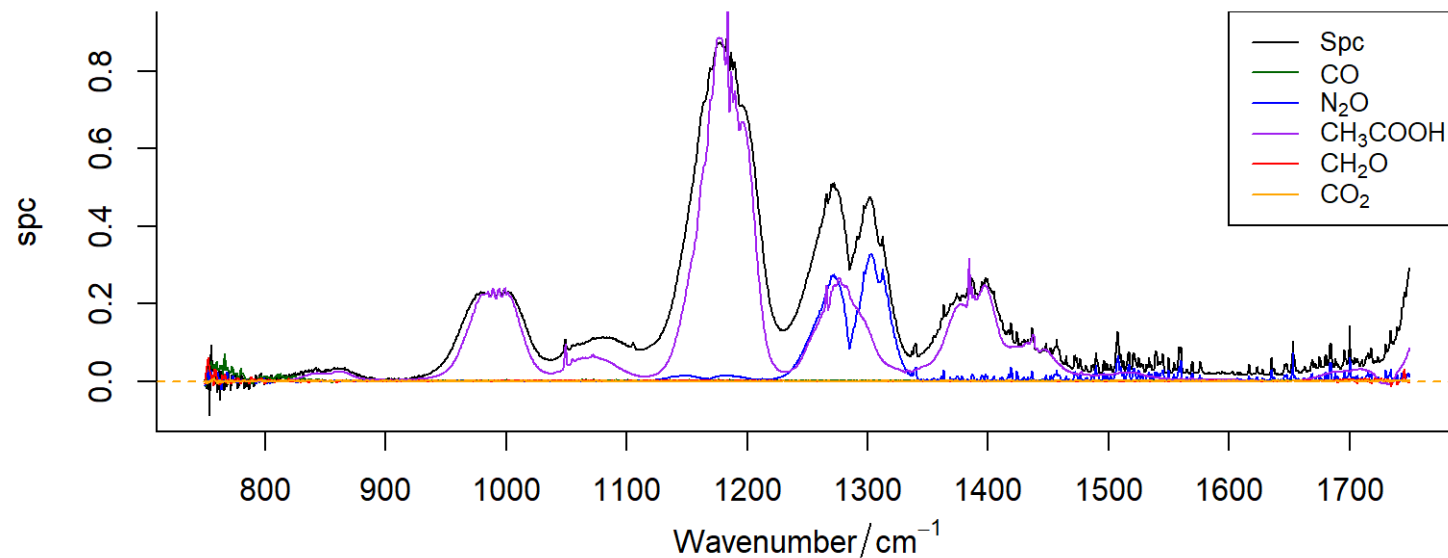
- N₂ with Helium tracer
- Dekati Dilution system



FTIR



NOx – high concentration

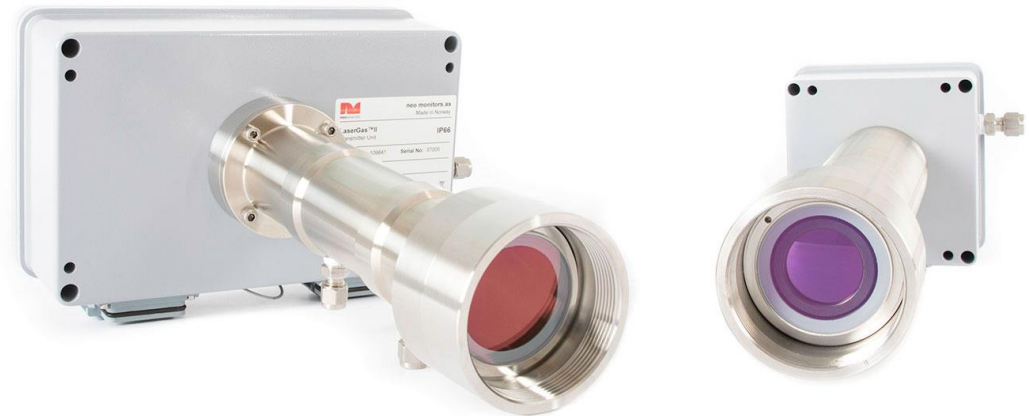




Liquid Gas mixer , HF and CF4 laser



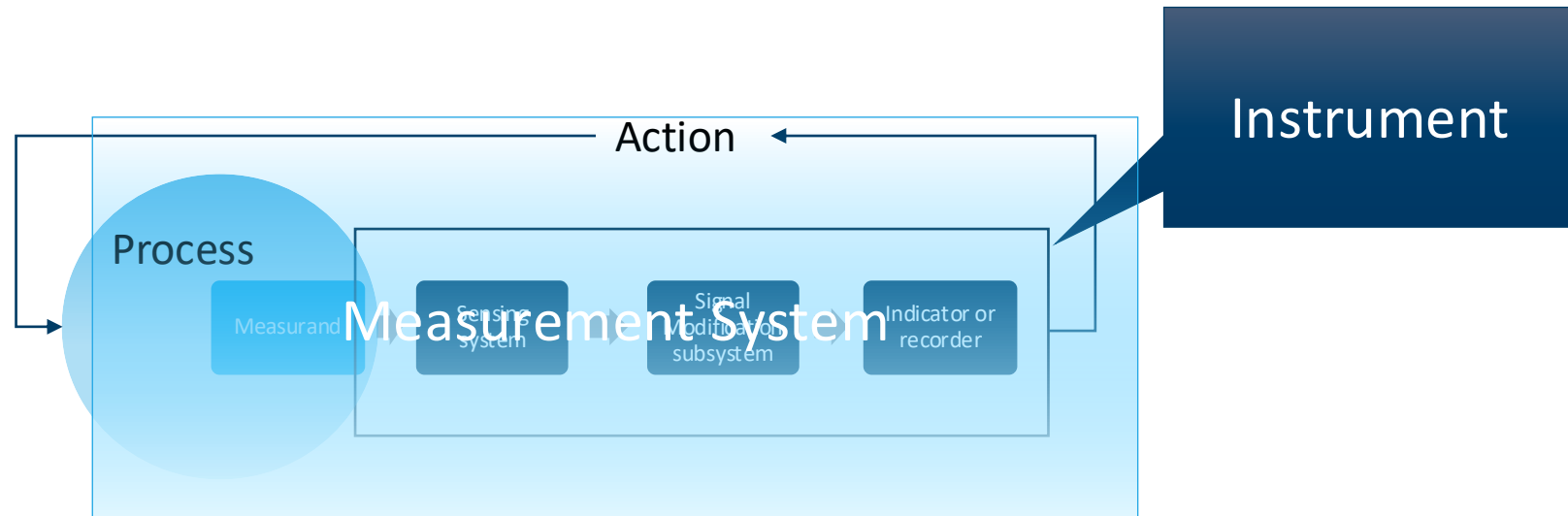
- CF4 laser: Methane H2O interferences
- infrared tunable diode laser absorption spectroscopy.



Measurement group -

Measurements systems are an important part of the production process and more than just the instrument.

- Measurements are necessary to monitor production process outcomes.

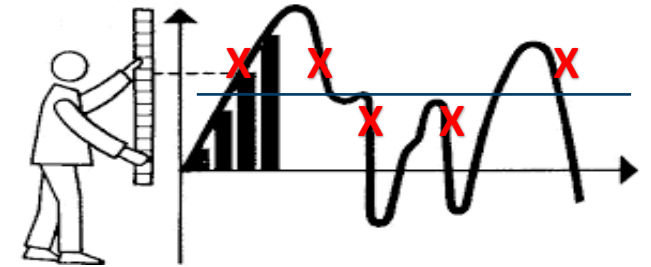


Measurement systems

MS ...more than just the instrument ...

Sampling must be representative with respect to.

- suitable measurement site, time, operational conditions
- number, duration, extend of measurement
- operator ...

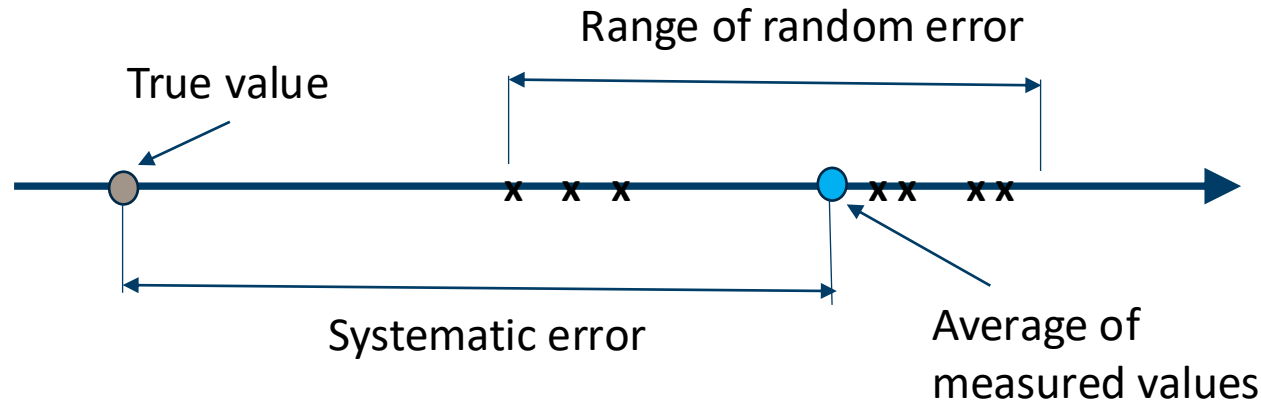


Emission measurements in flowing gases require defined flow conditions (geometry of gas piping) at sampling location.

NB! Sample line, sample handling, preparation and analysis are an important part of the measurement system

Measurement Systems - Challenges

Repeated measurements of the same item do not always give the same value.



Measured value $Y = X + E$ where X is the true value and E is the measurement error

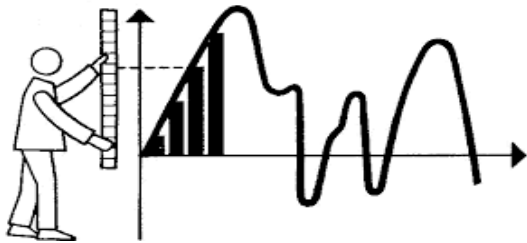
Some variation in the process outcome may occur due to the error in the measurement system.

- The process of measuring itself has variation and can produce "defects"!

.... heard that before ?

“You can see a lot by just looking”

Lawrence Peter "Yogi" Berra

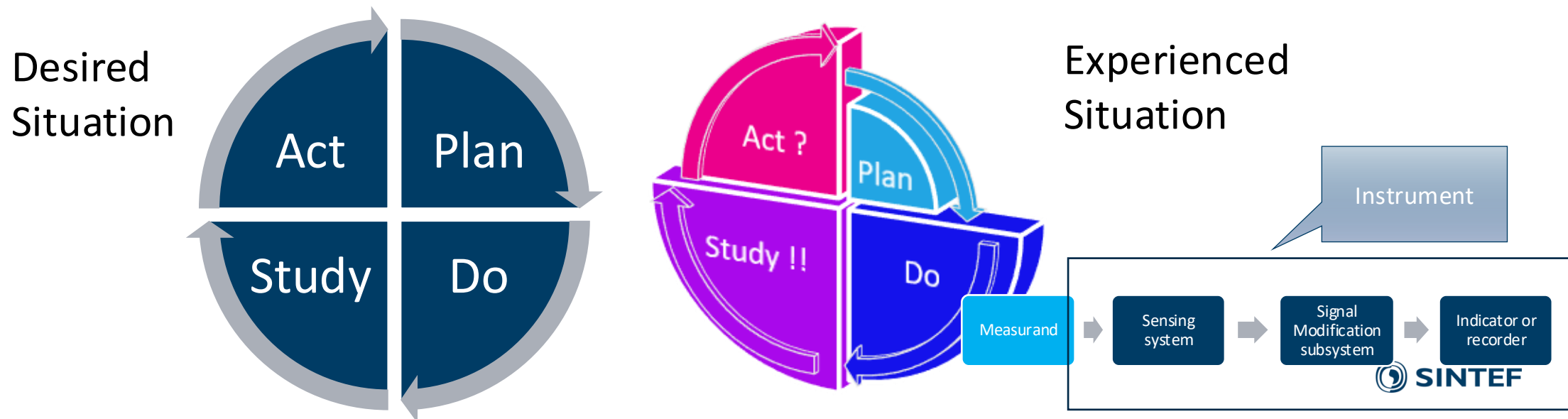


"You can generate a lot of data by just measuring"

However,...

..measuring should **generate useful information** giving a basis **for decision making**.

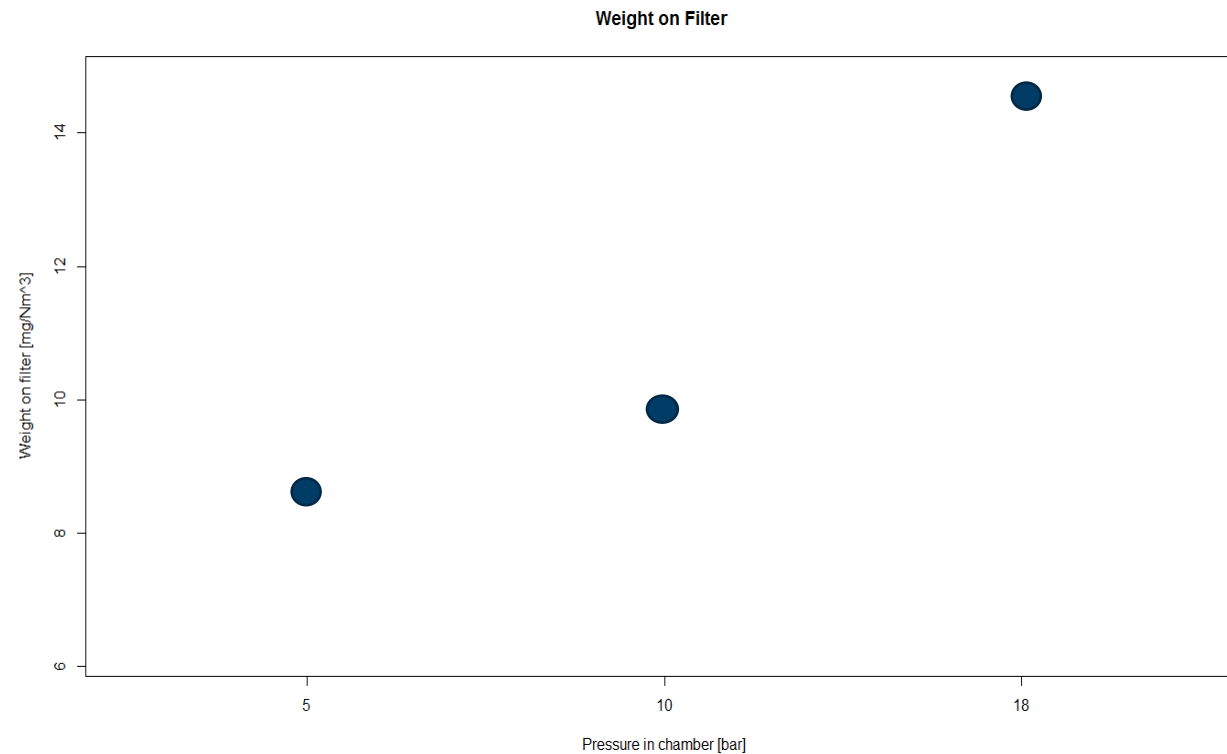
- Measured data (observation) have to be put in context to make sense!



Measurement planning to evaluate process improvements

Use basic principles of experimental design

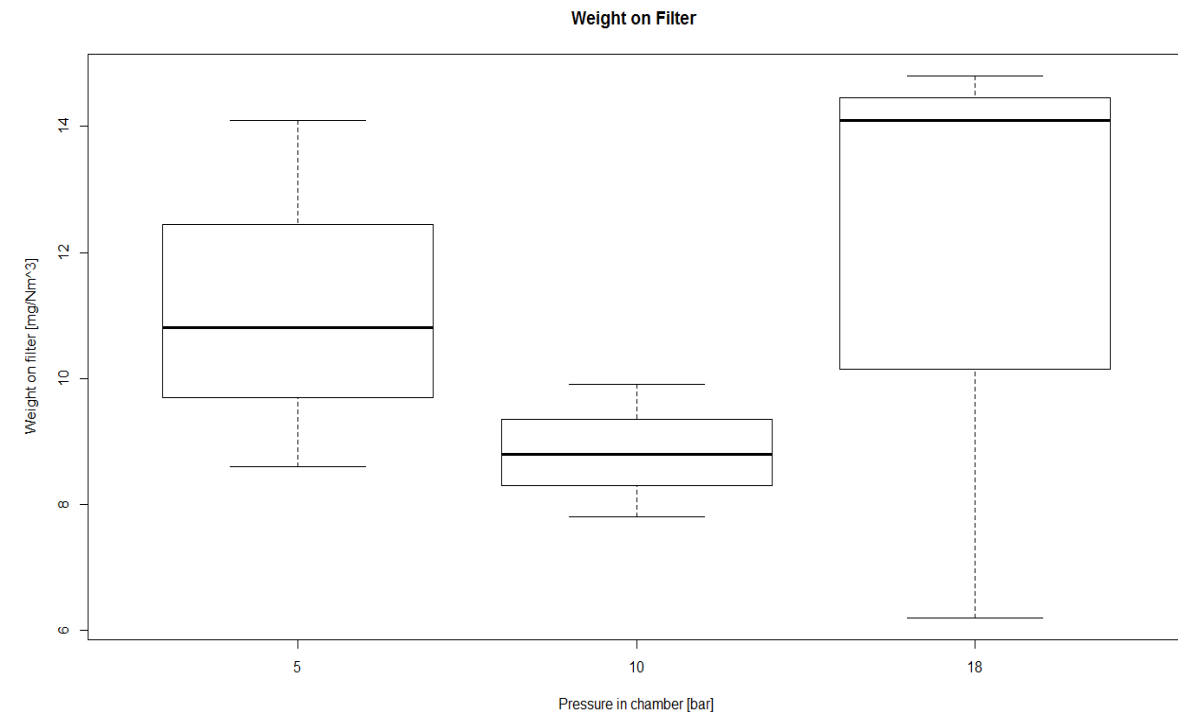
- **Replication** is necessary to obtain an estimate of the experimental error σ_E^2



Measurement planning to evaluate process improvements

Evaluation of process improvements requires **proper measurement planning** to compare

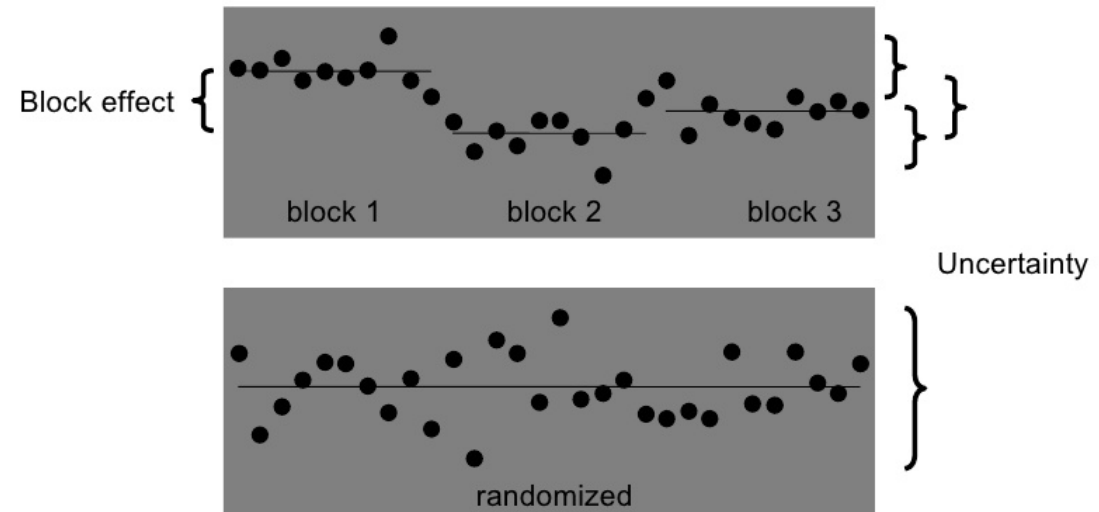
- the **variation between treatments** (variation between treatment means)
- to **variation within the treatment** (difference in observations within a treatment from the treatment average).



Measurement planning to evaluate process improvements

Use basic principles of experimental design - Industrial Trails

- **Replication** is necessary to obtain an estimate of the experimental error σ_E^2
- **Randomization** is necessary to averaging out extraneous factors – observations should be independent distributed random variables. Eliminate potential confounding between design and run-order
- **Blocking** is used to reduce or eliminate variability of factors that may influence the response but in which we are not interested



Measurement planning to evaluate process improvements

How to start:

Recognition and clear statement of the problem !!!

- Define what to measure and risk access your choice of factors, levels, and ranges

Measurement planning should involve – MS key personnel

- Process operations
- Measurement group
- Laboratory

Does the measured response reflect the state of the production! Right indicator?

5M: Tool to access factors affecting a measurement system

What can go wrong?

- Man: Operators skills
- Machine: Measuring instruments (gauge) itself
- Material: Specimen and chemicals for preparation
- Method: Test specification (experimental parameters, specimen preparation, sampling plan, etc).
- Milieu: Environment (temperature, humidity, etc.)

Measurement planning

Choice of factors levels and ranges

Consider factors that influence the process or system response and **classify the factors** as either

- **Potential design factors** (factors the experimenter wants to vary) or
- **Nuisance factors** (factors that may have large effect yet not of interest in the context of the present experiment)

Potential design factors are further broken down to

- **(Actual) design factor** (factor selected for study the response in experiment, controllable)
- **held-constant factors** (variables that may exert effect on the response but held to a constant level because it is not of interest for particular study)
- **allowed-to-vary factor** (variables that may not have an influence on the response – make sure that these are thoroughly risk assessed)

Nuisance factors are further broken down to

- **controllable** (level can be set by experimenter – Blocking e.g. batch of materials)
- **uncontrollable** but measurable (to treat it as a covariate. E.g. humidity in process environment)
- **noise factors** (factor that varies naturally and uncontrollable in the process.)

The experiment has to find settings for the controllable design factors to minimize the variability transmitted by the noise factors

Measurement planning in conclusion

Challenges

Outsourcing: External partners conducting measurements - Key competence transfer ?

- knowledge about process peculiarity has to be transferred from internal key-personnel to external measurement group.

-> even more important to conduct proper measurement planning!

Worth evaluating the cost for, and quality of measurement

- - Outsourcing a good "Bargain"? Ask the ones using external measurements to control their process.

To improve processes it is important to

understand the "measurement system" and its interdependencies.

- Good practice to secure and improve quality of measurements is to involve personnel using measurement data in the process of generating measurement data.

Measurement planning in conclusion

Spend time on identifying the challenges related to measuring a specific response

- Design and risk access and your measurement campaign
 - Choice of factors levels and ranges

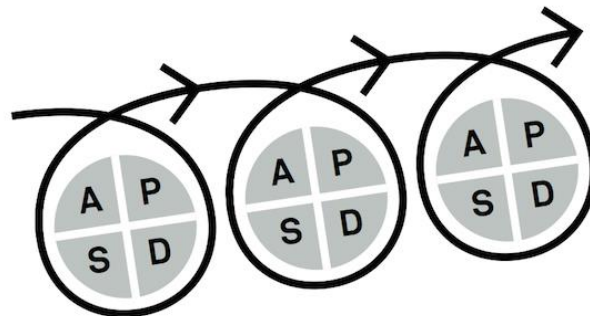
(Support from SFI NTNU SINTEF)

Implement the basic principles.

-> Produce useful data by putting your observations into the right context!

Continuously improve

- -> Lessons learned





Teknologi for et bedre samfunn