The advantages of using Dynamic reference standards

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MetroHyve/Hydraite Workshop
Delft, 2019-09-11

Overview

- The advantage and disadvantages of dynamic reference standards
- The developments in MetroHyve

Measurement challenge

- What can be considered as a dynamic reference standard versus a dynamic calibration method?
- ISO1645 describes many different dynamic blending methods but applying the standard does not necessarily make a dynamic reference standard

NPL Multi-gas, Multi-pressure Standard Humidity Generator

- Dynamic humidity calibrations in “industrial” conditions.
- Non-air gases (e.g. hydrogen, methane, synthetic natural gas, CO_2, argon)
- Pressures up to 3 MPa (30 bar)

- Hybrid generator able to generate values in single pressure dew-point temperature generation mode from -60 ºC to +15 ºC
- Ability to mix gases using array of mass flow controllers

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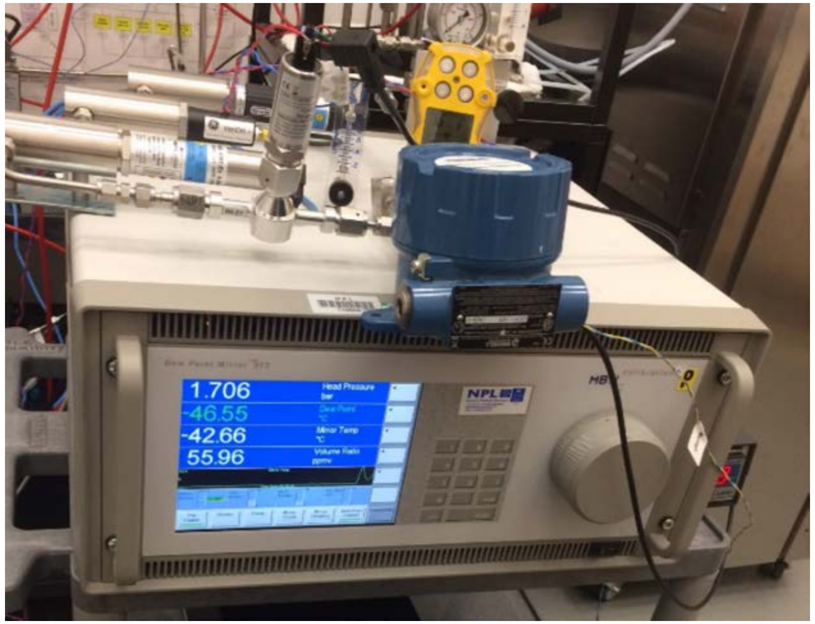
MetroHyVe Hygrometer study

- Six commercially available metal-oxide hygrometers loaned by collaborators were tested by comparison against the NPL Multi-gas, Multi-pressure Standard Humidity Generator:

  - Calibrations performed in nitrogen and hydrogen:
  - at pressures of 0.17 MPa and 2 MPa
  - at dew-point temperatures from -65 °C to -20 °C
  - corresponding to amount fractions of water vapour from 0.5 μmol mol^{-1} to 50 μmol mol^{-1} at 2 MPa
  - generated uncertainty typically ±0.12 °C



- Summary of findings in online gas analysers session.

Novel method of H_2O reference cylinder production with primary traceability

- Novel method developed to transfer NPL Multi-gas, Multi-pressure Standard Humidity Generator traceability to binary H_2O in hydrogen gas mixtures in cylinders.
- MetroHyVe research target mixtures with reference value of 5 µmol mol^{-1} water vapour content in hydrogen.
- Tests of the long-term stability of the reference gas mixtures will inform the uncertainty that can be associated with the reference values.

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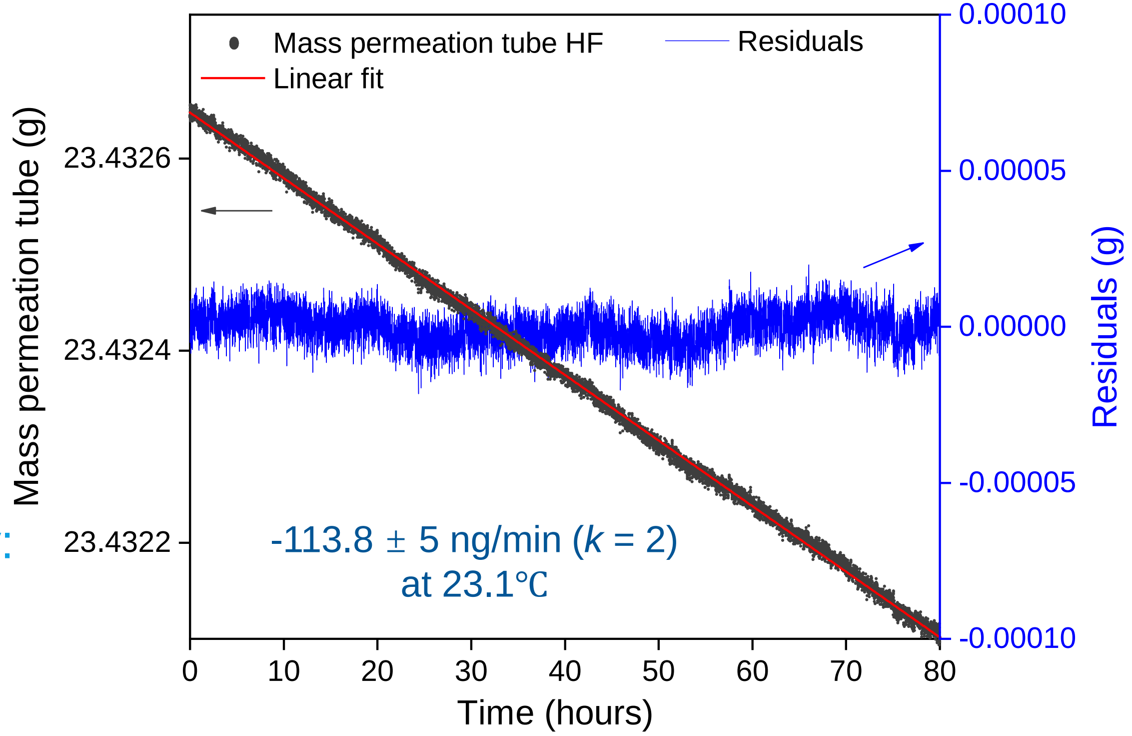
Permeation-based gas generation method (ISO 6145-10)

- Calibrated and passivated MSB (TA Instruments)

Temperature ± 0.02 ℃
Pressure ± 0.1 mbar
Flow rates ± 1.5 mL/min
Stabilization period ± 3 days

→ Mass measurement stability: ≤ 3 µg over 5 days

- Permeation rate (q_m) = mass loss per unit of time



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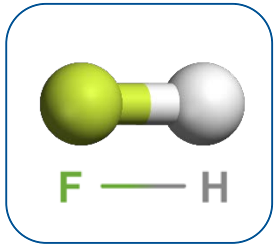
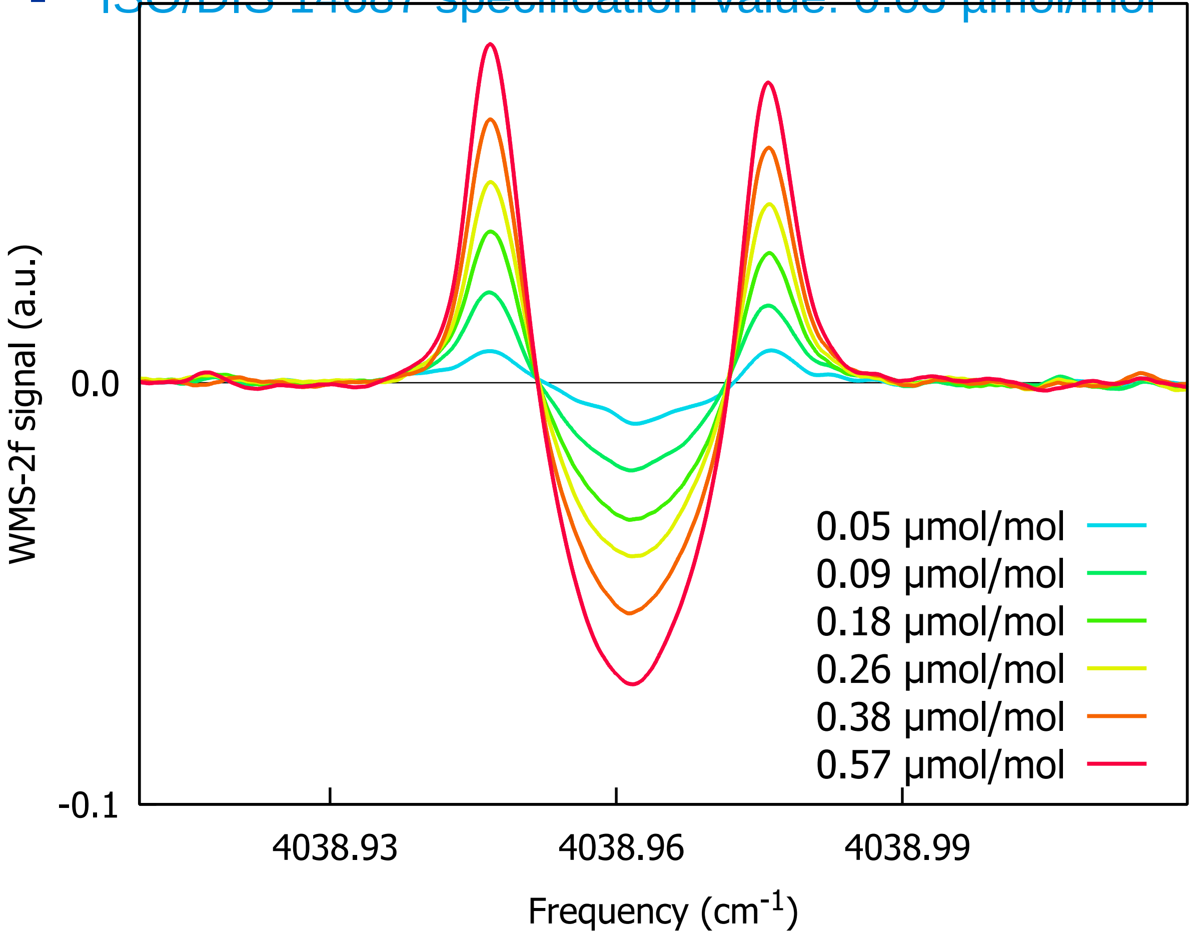
Hydrogen fluoride



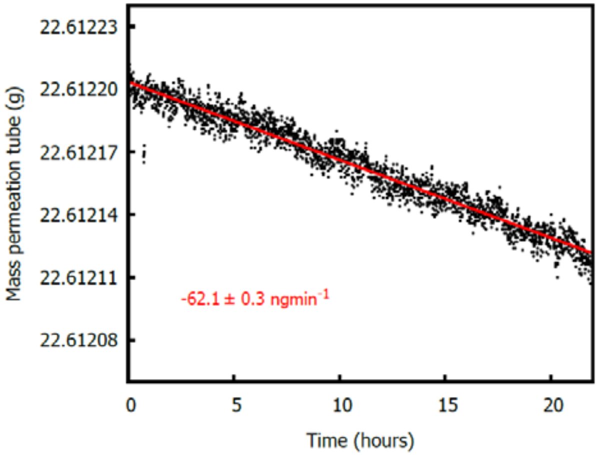
- ISO/DIS 14687 specification value: 0.05 µmol/mol

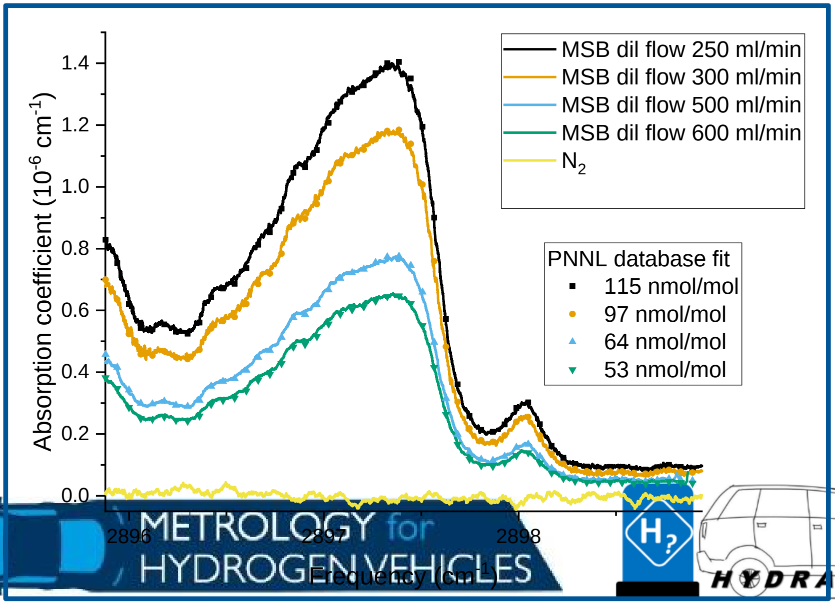


- HF in H_2 can be analysed in the nmol/mol and lower µmol/mol range
- Preliminary results indicate that the method is sufficiently sensitive to analyse HF in H_2 samples according to ISO 14687-2

Dilution system for formaldehyde

- Generated formaldehyde using a MSB with permeation tube (Fine Metrology).
- Generated different amount fractions around the ISO 14687-2 threshold (0.2 ppm) by changing the dilution flow and/or permeation chamber temperature.
- Measurement by CRDS.
- Purity of the permeating gas still needs to be analyzed (some water is expected).





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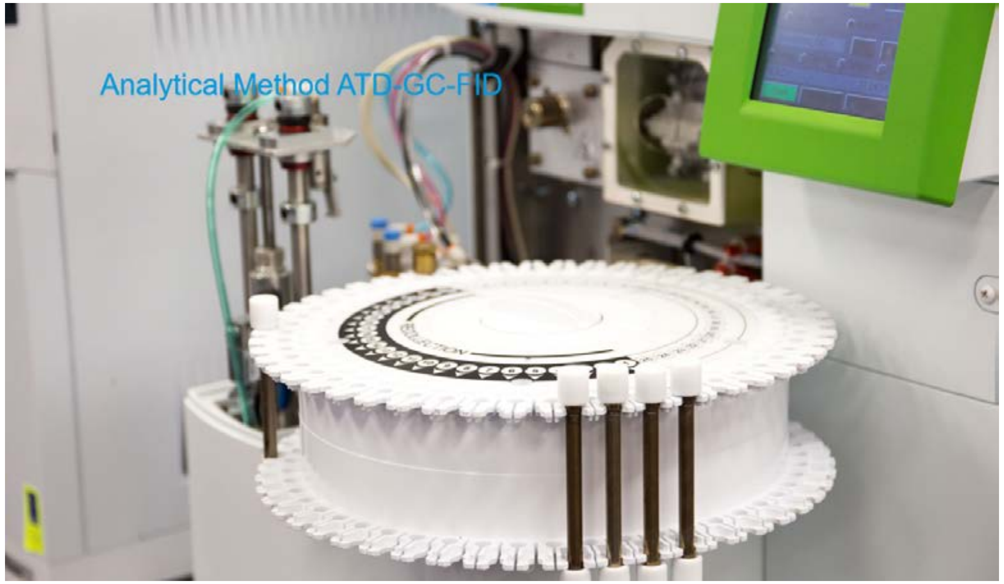
Use of sorption tubes

- Can be prepared in a lab and taken to the place of analysis
- Depending on the expected concentration of the impurity more gas can be flushed through the tube to gain a reasonable amount for analysis
- Direct sampling at HRS is difficult due to the high pressure of the H_2

- Disadvantage: they can only be used for one analysis; then they have to be conditioned and loaded again

Sorbent tubes for short term stability test

- Sorbents
  - Tenax TA
  - Carboxen 1003
  - Dual bed sorbent trap – Tenax TA & Sulficarb
- Sulfides
  - H_2S – was not trapped on the sorbent materials
  - CH_4S – was not trapped on the sorbent materials
  - COS
  - CS_2
  - THT
  - T-BM
  - n-Hexane as internal standard



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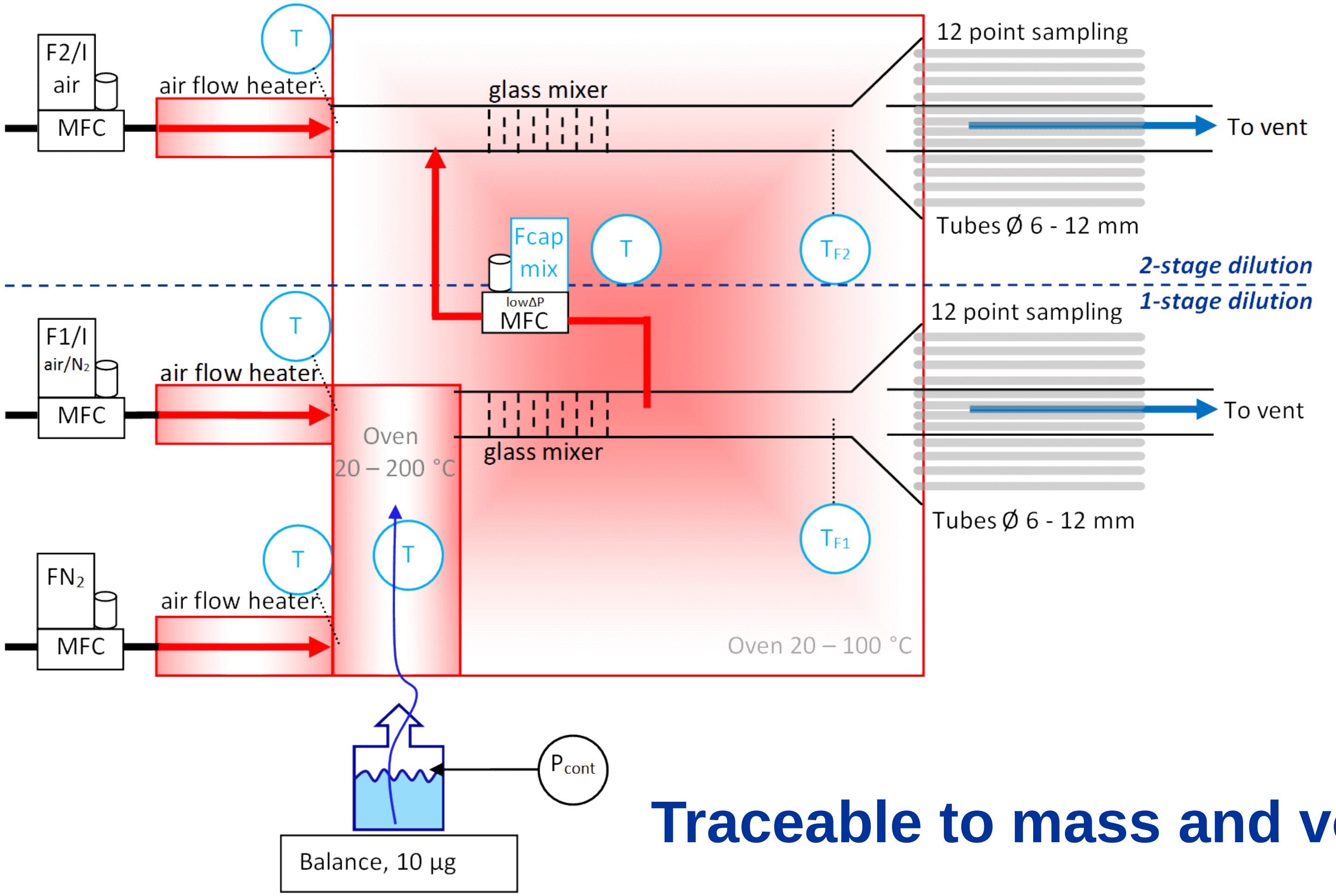
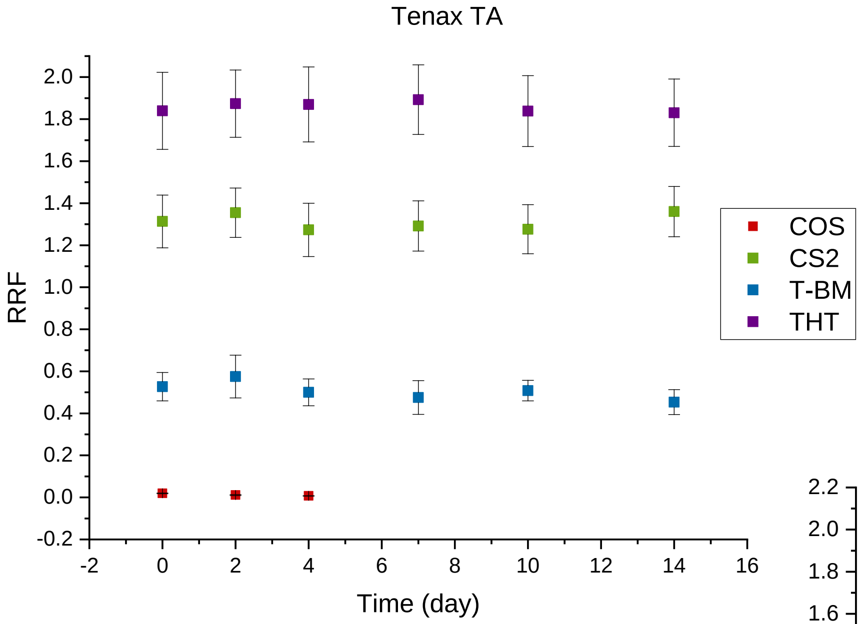
ISO 16017-1
Pumped sampling

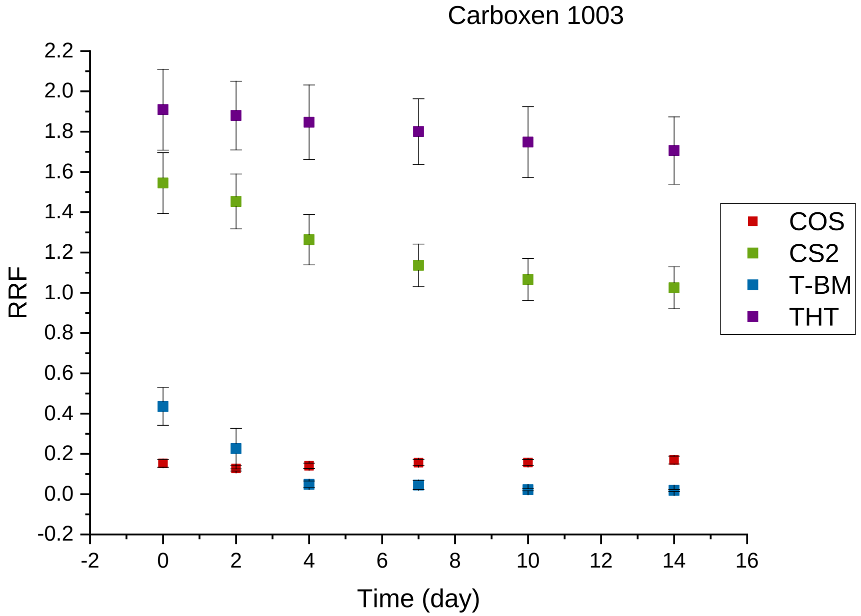
Schematic drawing dilution system

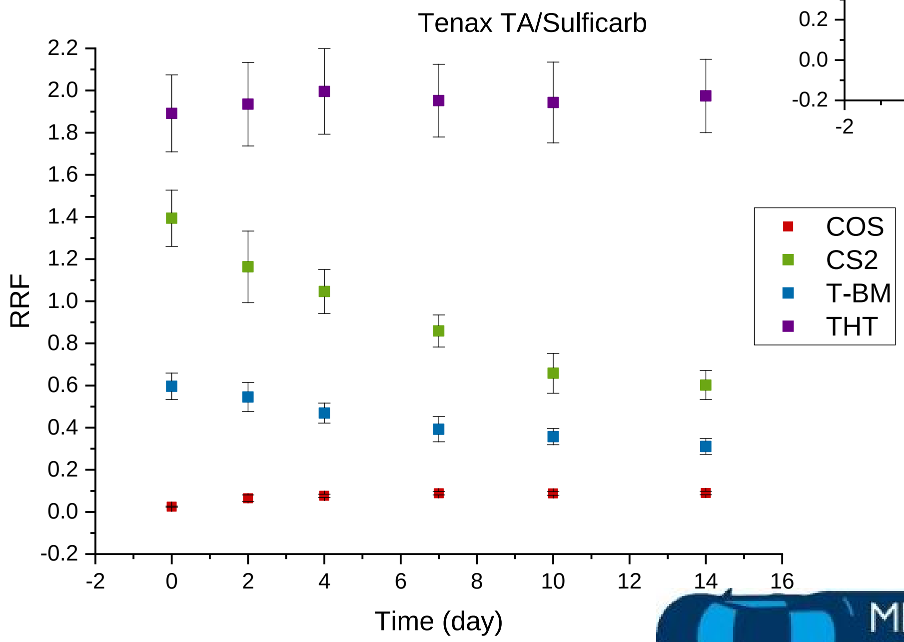


Traceable to mass and volume

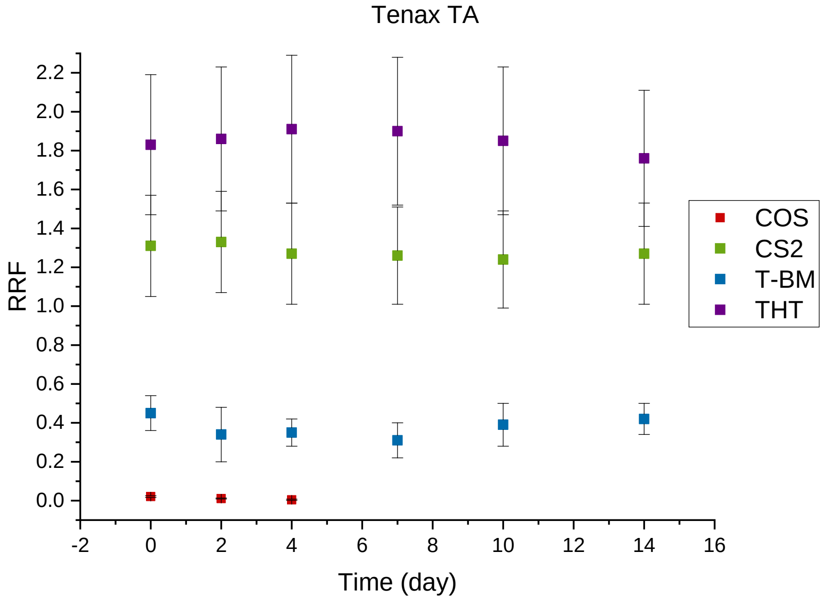
Short term stability sulphides on different sorbents (~ 140 ng)

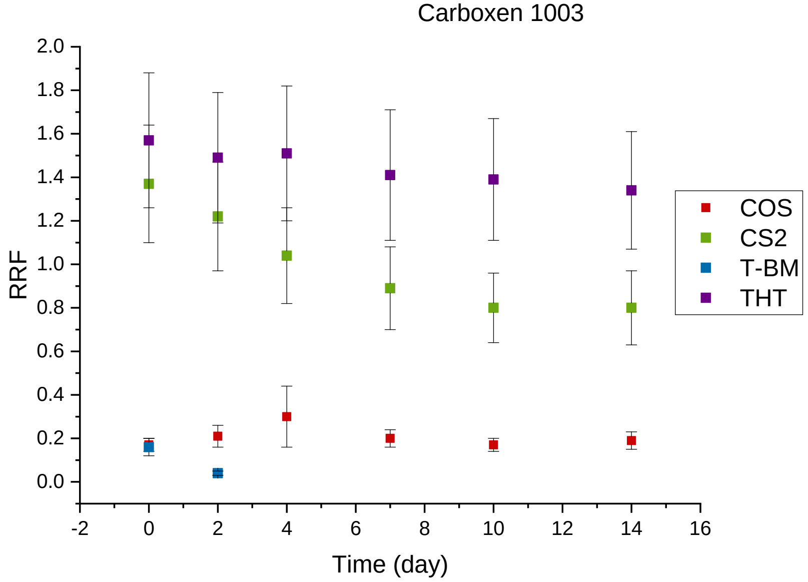


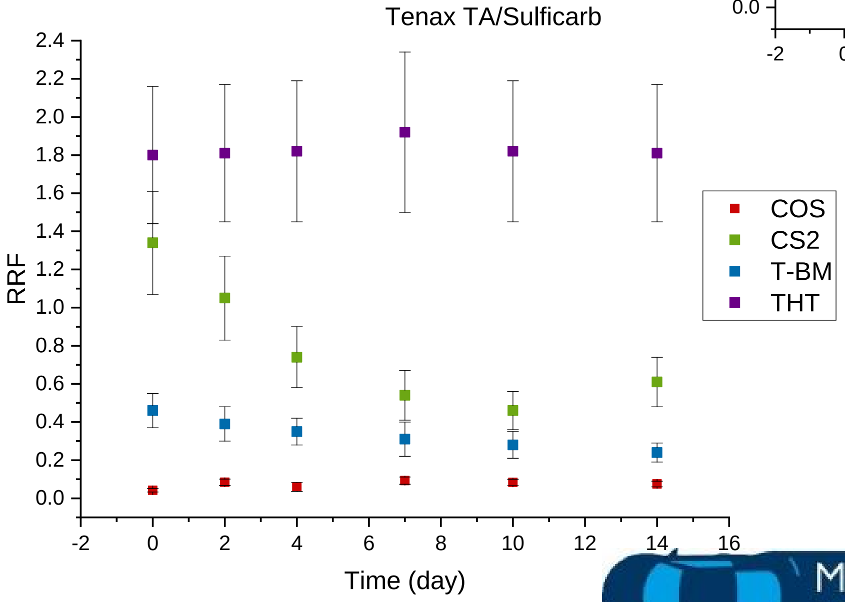




Short term stability sulphides on different sorbents (~ 28 ng)







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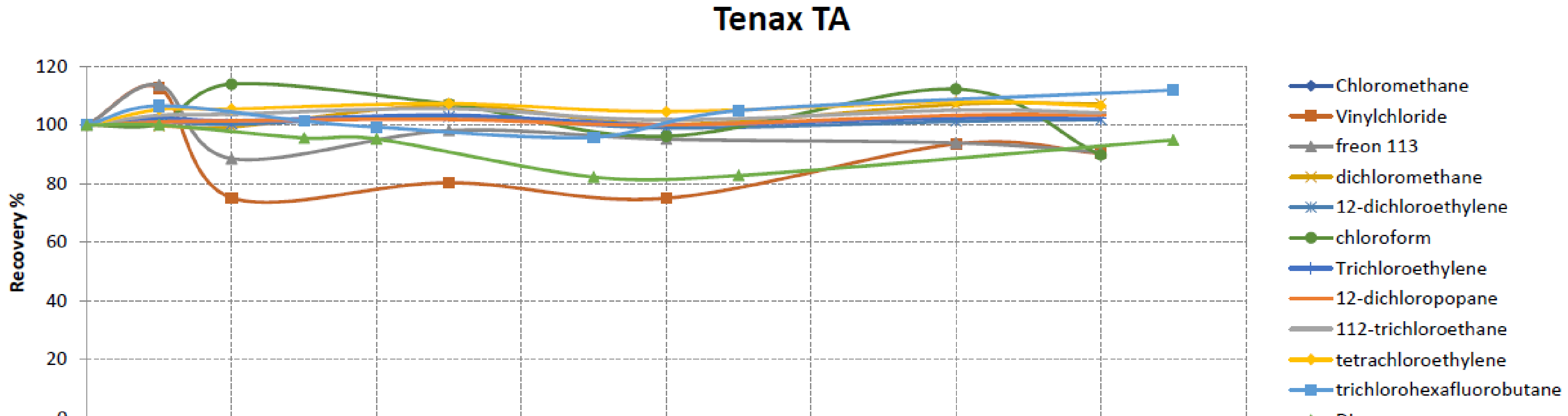
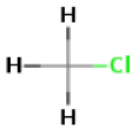
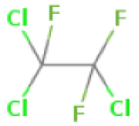
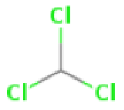
Short term stability for different halogenates (1)









Chloromethane
BP = -26ºC

Vinylchloride
BP = -14ºC

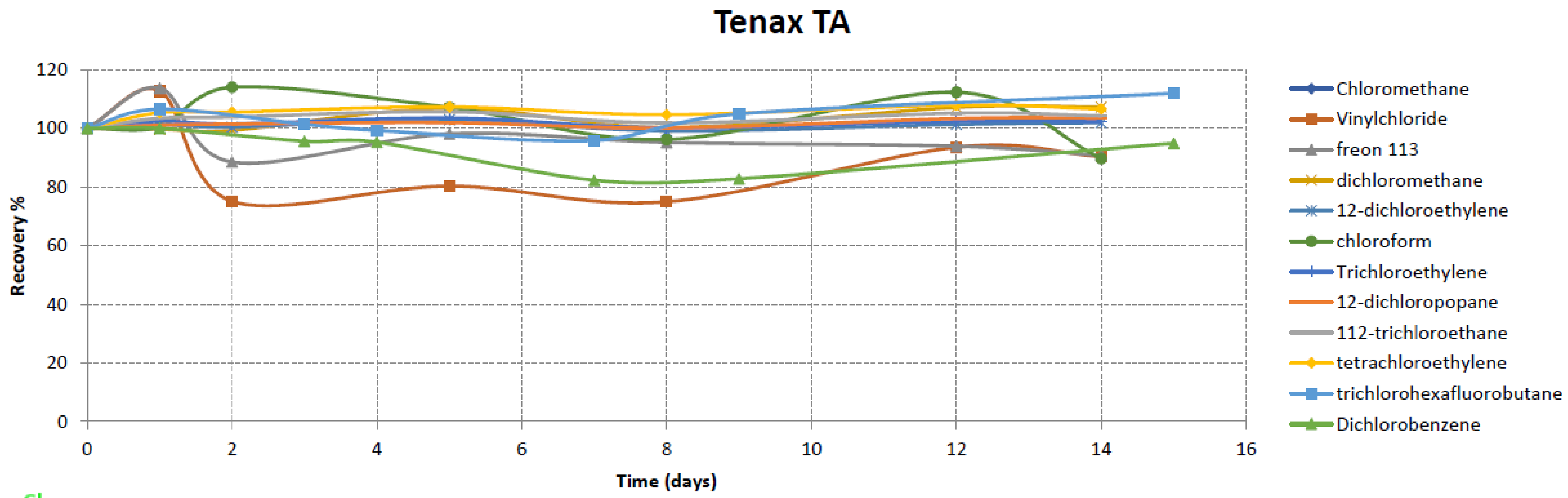
Dichloromethane
BP = 40ºC

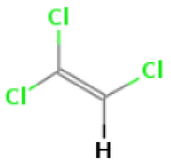
Trichlorotrifluoroethane
BP = 48ºC

Dichloroethylene
BP = 55ºC

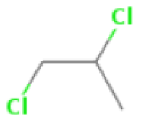
Chloroform
BP = 61ºC

Short term stability for different halogenates (2)

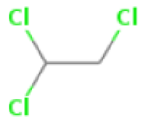




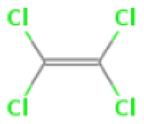
Trichloroethylene
BP = 87ºC



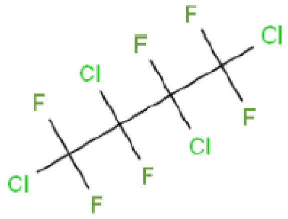
Dichloropropane
BP = 97ºC



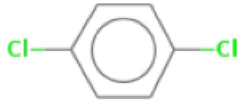
Trichloroethane
BP = 114ºC



Tetrachloroethylene
BP = 121ºC

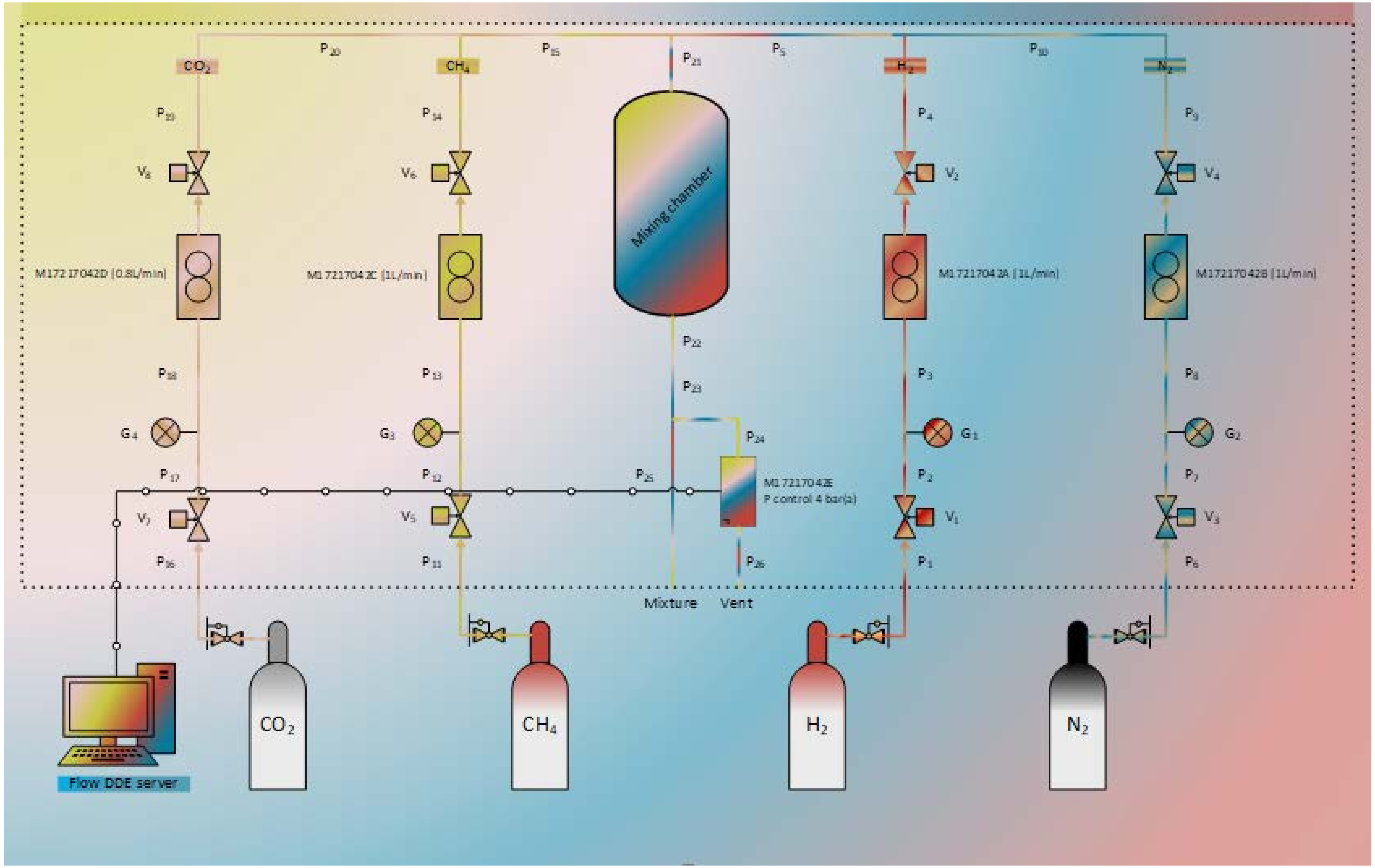


utane



Dichlorobenzene
BP = 174ºC

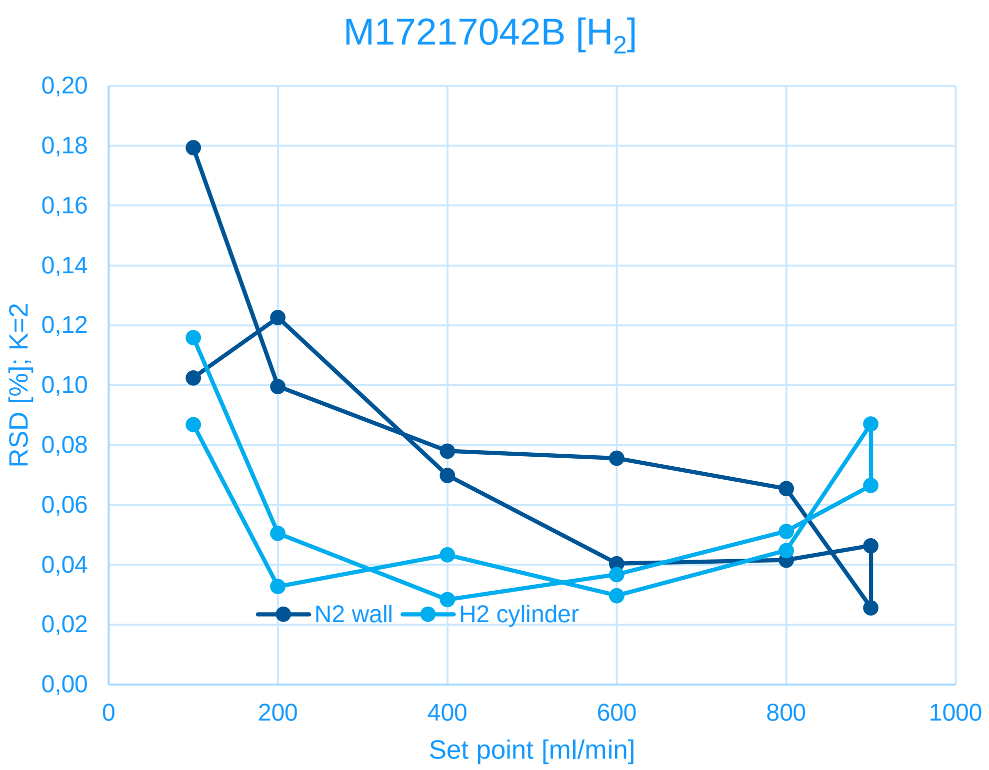
Schematics of the mixing station developed at VSL



Initial results

Gas	MFC actual [ml/min]	Mixed actual [%]	GC AA1234 [%]	AA1234 D [%]	GC AA1235 [%]	AA1235 D [%]
N_2	58.72	18.05	18.202	0. 83	18.188	0.75
CO_2	48.33	14.86	14.996	0. 94	14.967	0.74
CH_4	206.11	63.36	63.399	0. 05	64.054	1.09
H_2	12.12	3.73	3.403	-8.7	2.791	-25
		$N_2+CO_2+CH_4$	96.597	$N_2+CO_2+CH_4$	97.209	

- 3 of the 4 MFC operated under 20% FS
- Verification performed against VSL gravimetric standards
- AA1234 average of 10 injections at 3 barA
- AA1235 average of 6 injections at 4 barA
- Testing on Hydrogen purity mixtures has yet to be performed



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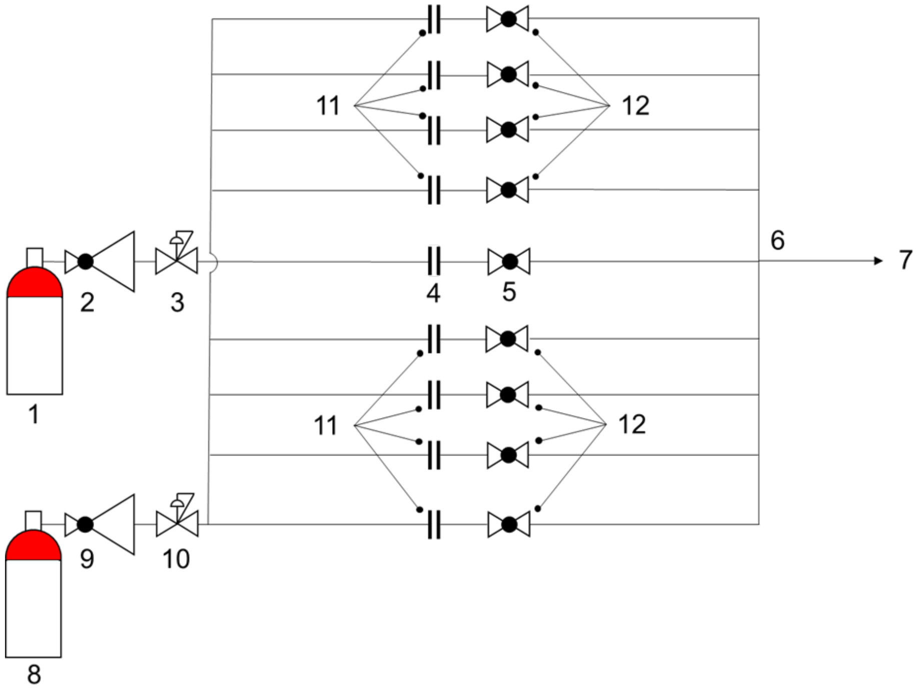
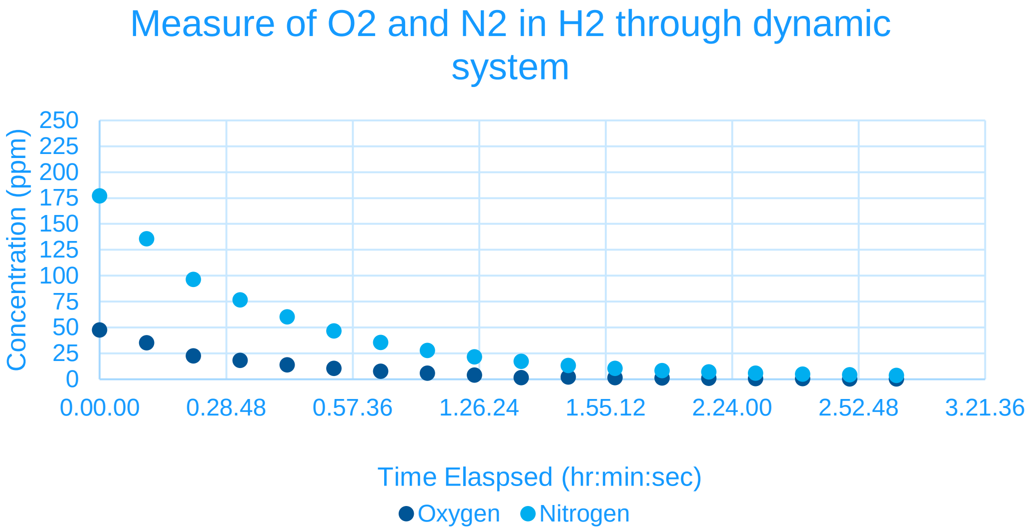
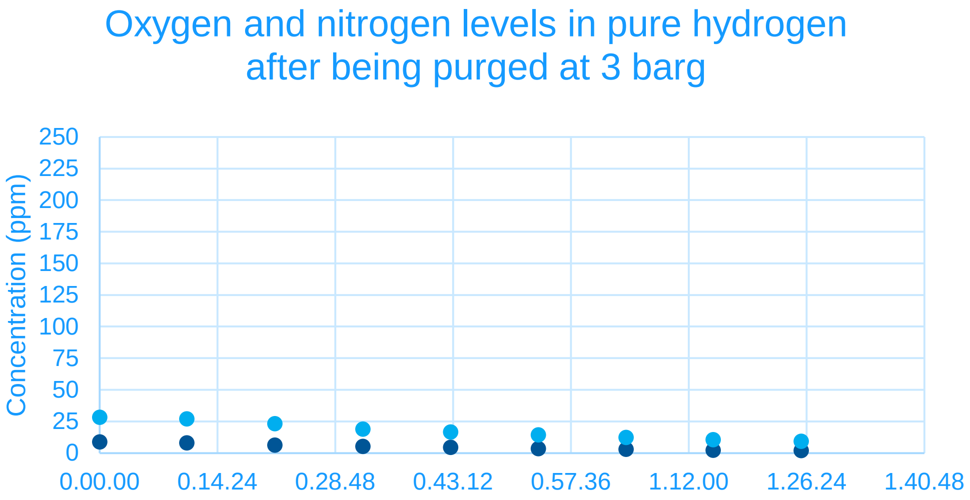
Purging on dynamic dilution systems







Purging method: flow through and at elevated pressures

Available resources

- A2.3.1 Hydrogen purity analysis: suitability of sorbent tubes for trapping hydrocarbons, halogenated carbons and sulfur compounds
- Reports on dynamic dilution system and purging will become available in due time
- ISO6145 is off course available at ISO

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

THANK YOU

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