PROMETH$_2$O

20IND06 PROMETH2O

Metrology for trace water in ultra-pure process gases

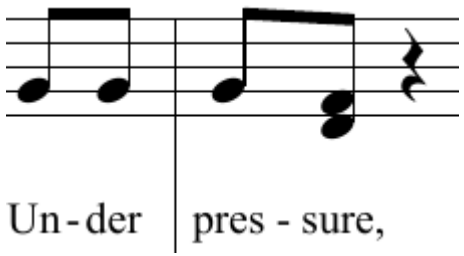
FinalWorkshop

Gas Analysis 2024 Symposium / Porte de Versailles, Paris - France

Tuesday 30th of January 2024

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

Novel reference standards to provide measurement traceability in the part-per-billion regime



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Objectives

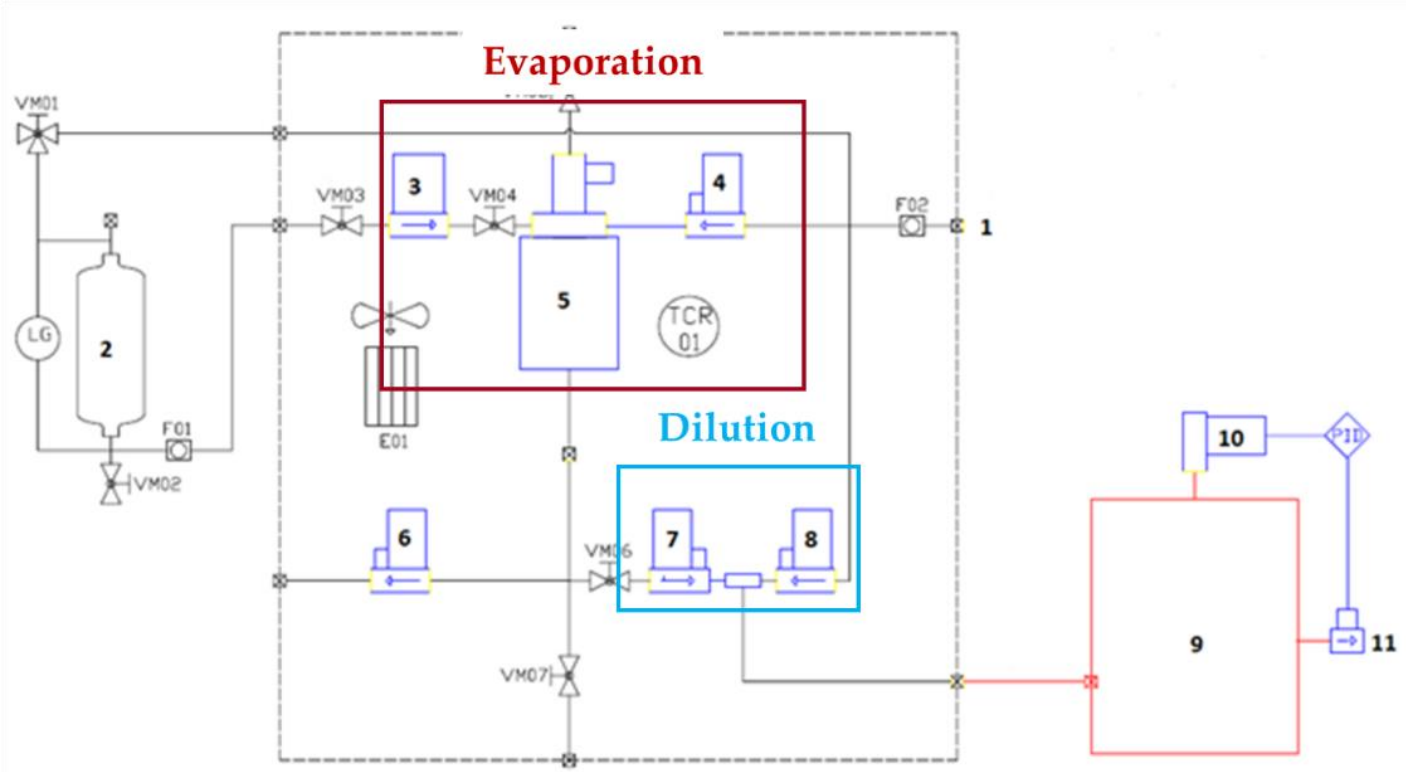
- at ultra-low humidity – a lack of harmonized measurement standards
- standards that underpin key technology areas such as **trace water measurements** in **ultra-pure process gases**
- **trace water is** the single largest matrix **contaminant** in ultra-high purity (UHP) process gases (e.g. Ar, N_2 and H_2)
- aim - to develop suitable **primary standards** for
  - the amount fraction range **from 5 ppm to 5 ppb** (-65 °C to -105 °C)
  - with a relative standard **uncertainty less than 3 % to 8 %**
  - in selected gas matrices of air, **N_2, Ar and H_2**
  - under pressures up to **1 MPa**

Current state-of-the-art

- Saturator based standard generators:
  - frost-point temperatures down to **-90 °C**
  - expanded measurement uncertainties **of the order of 0.5 °C**
  - at lower limit rarely, if at all, operate above the **atmospheric pressure** or with other gases than **N_2**
- Dilution, diffusion and permeation generators
  - all use additive methods of realisation, which depend critically on the **dryness of the initial gas supply**
- Coulometric Trace-Water Generators (CTWG):
  - currently cover the range from **20 ppm to 600 ppm**
  - with an uncertainty around 1 % of the value
  - have yet to be developed to reach their potential ultra-trace range **below 10 ppb**

Dilution Humid Air Generator

- Developed by **CETIAT**, France
- pressure range: 1 bar_a to 10 bar_a
- carrier gases: Air, Nitrogen, and Argon
- based on the dilution principle,
  also known as mixed flow generator

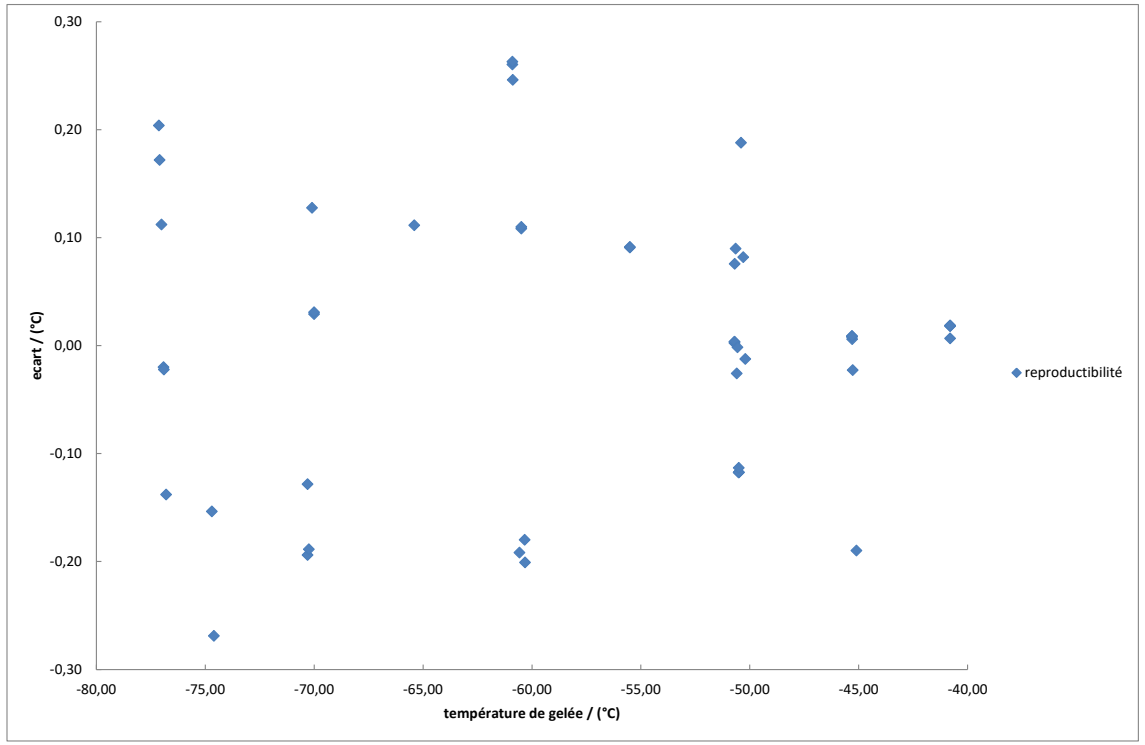


detailed scheme

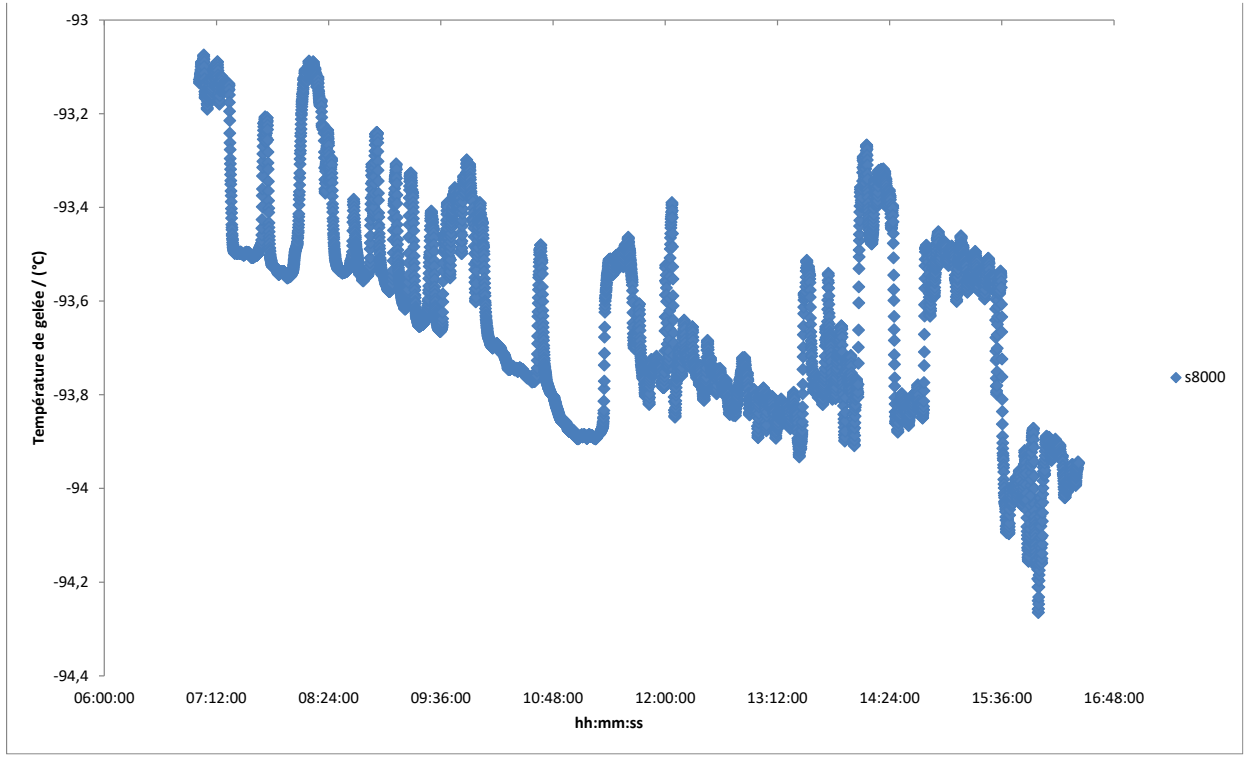
Dilution Humid Air Generator

Results

Reproducibility
(measured by MBW DP30)

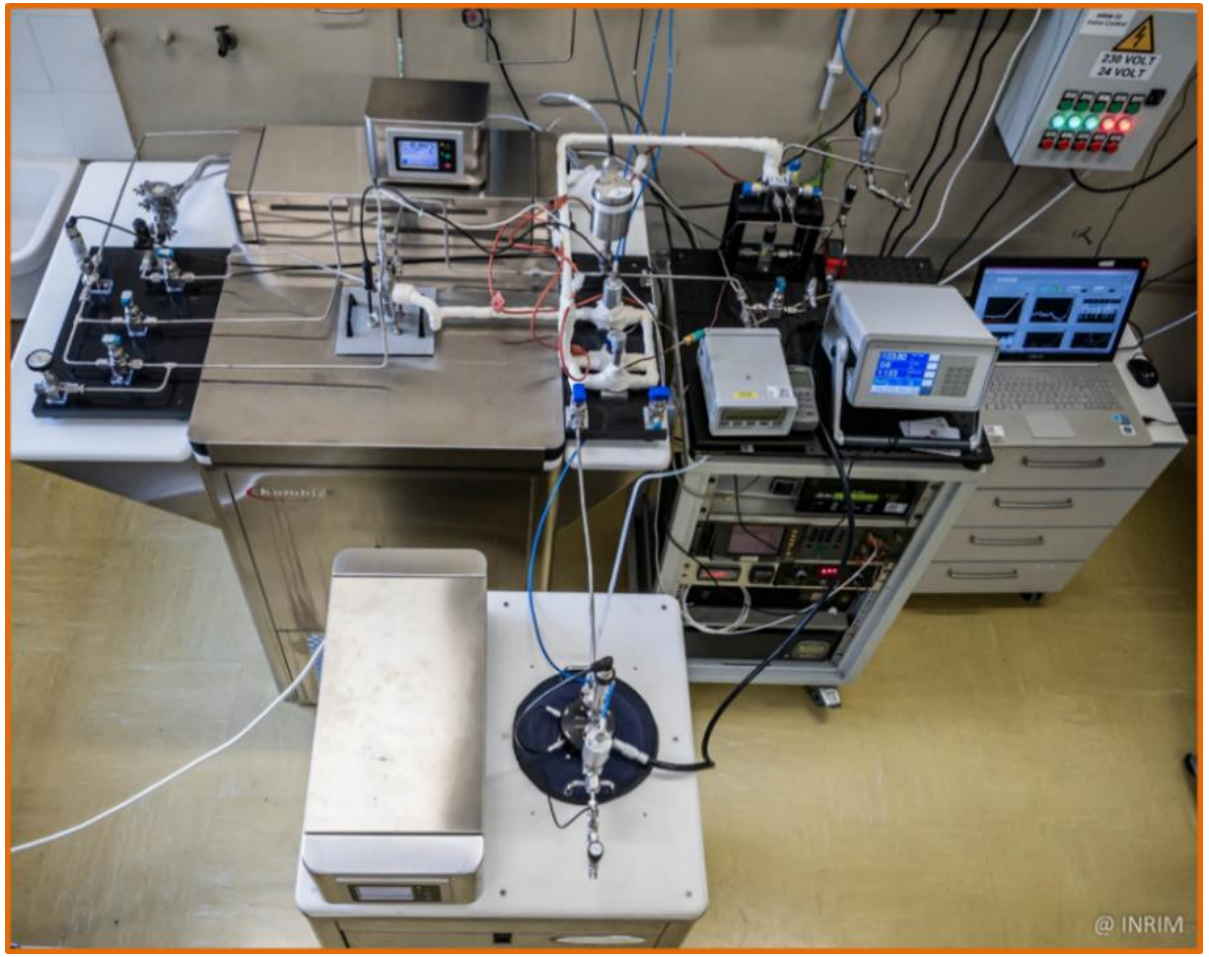


Dryness of the dry gas (molecular sieve): below -80 °C
Uncertainty: $U(k=2)$= 0,35 °C



Saturation-based generators

- Developed by **INRIM**, Italy
- operating principle (1T-2P), single-pass hum.gen.
- frost-point from **-105 °C to -20 °C**
- water vapour mole fraction between **5 ppb_v** and **1038 ppm_v**
- mole fraction $x_w = \frac{e_w}{p} = \frac{f(p_s,T_s)\cdot e_s(T_s)}{p_s}$
- carrier gases: Nitrogen and Argon
- pressure: **200 hPa to 6800 hPa**



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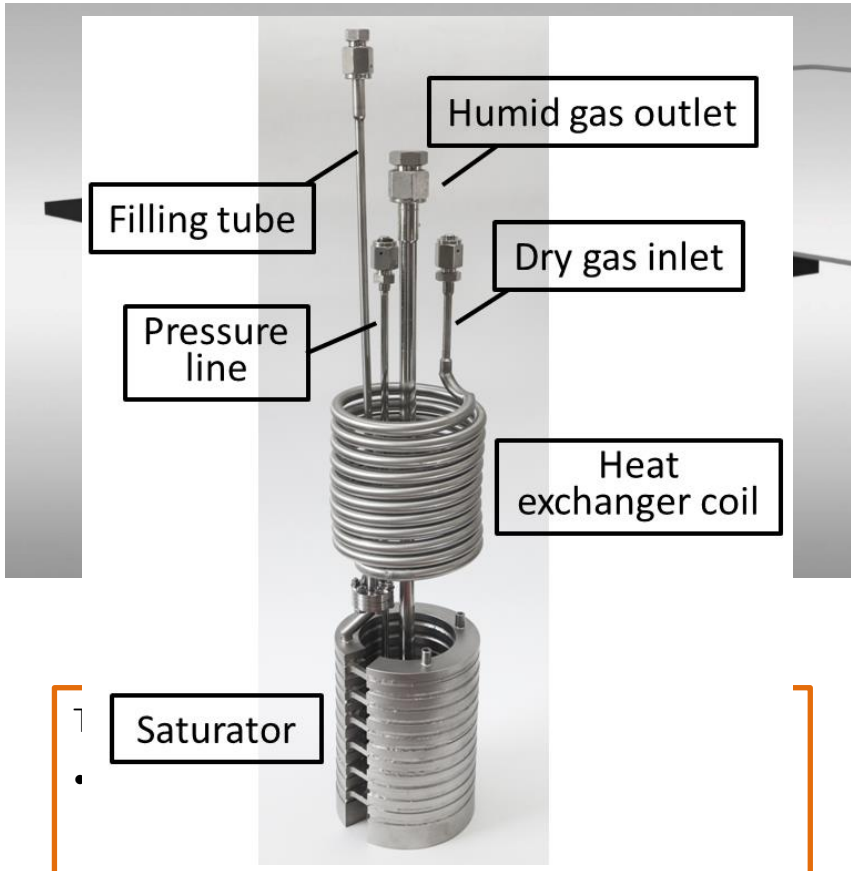
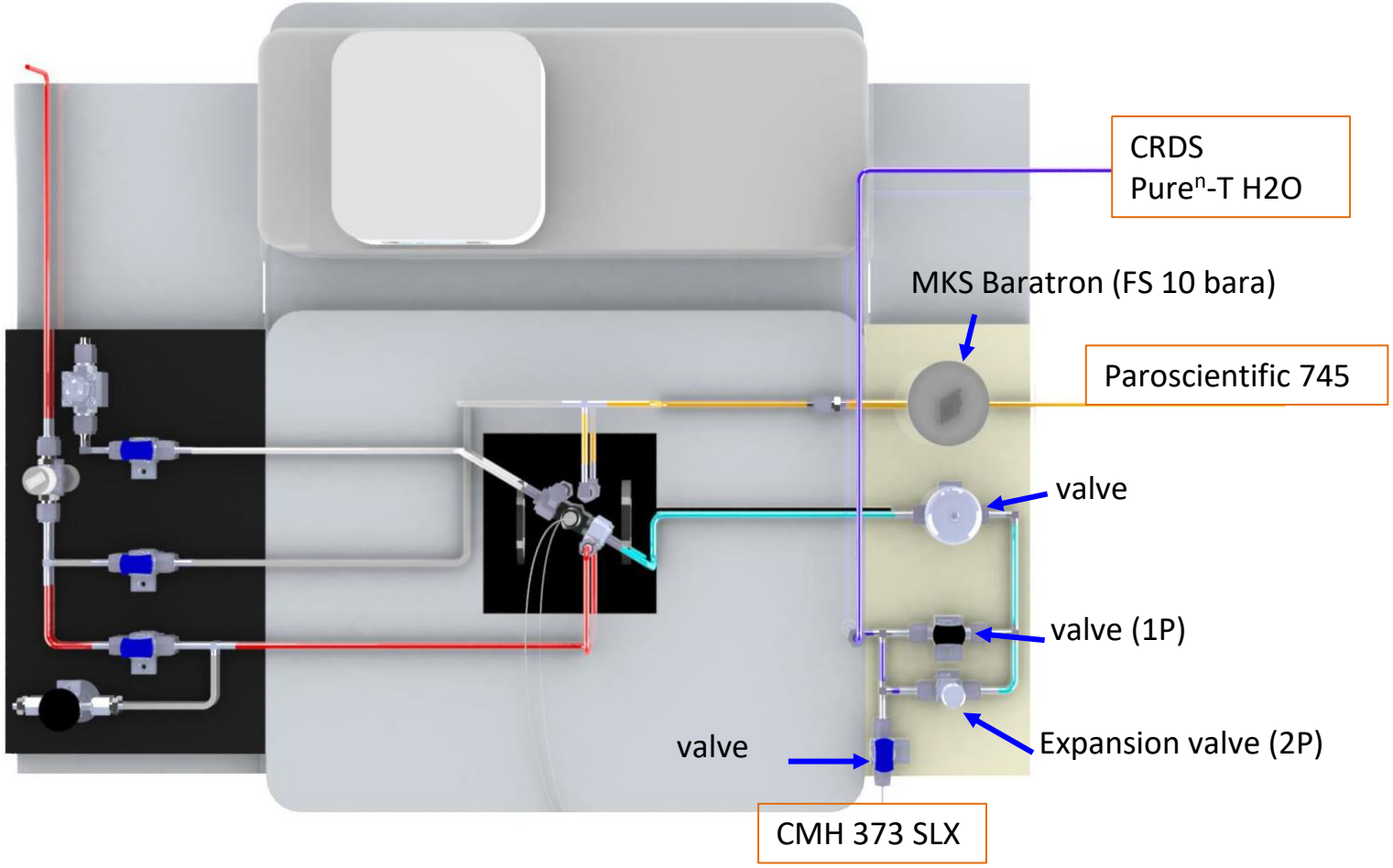


- CRDS: Photonics Technologies Pure^{n}-T H2O (0-20 ppm in N_2, LDL 200 ppt)



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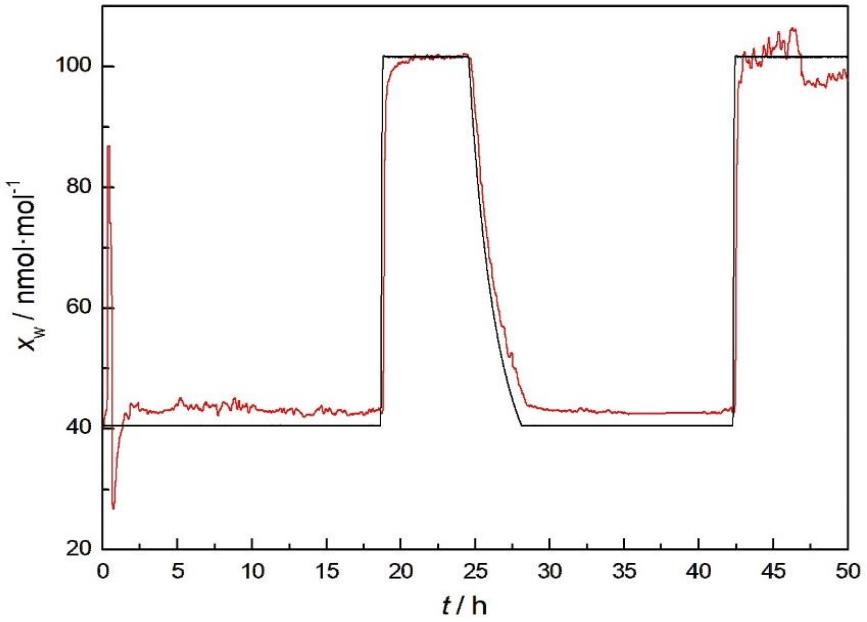
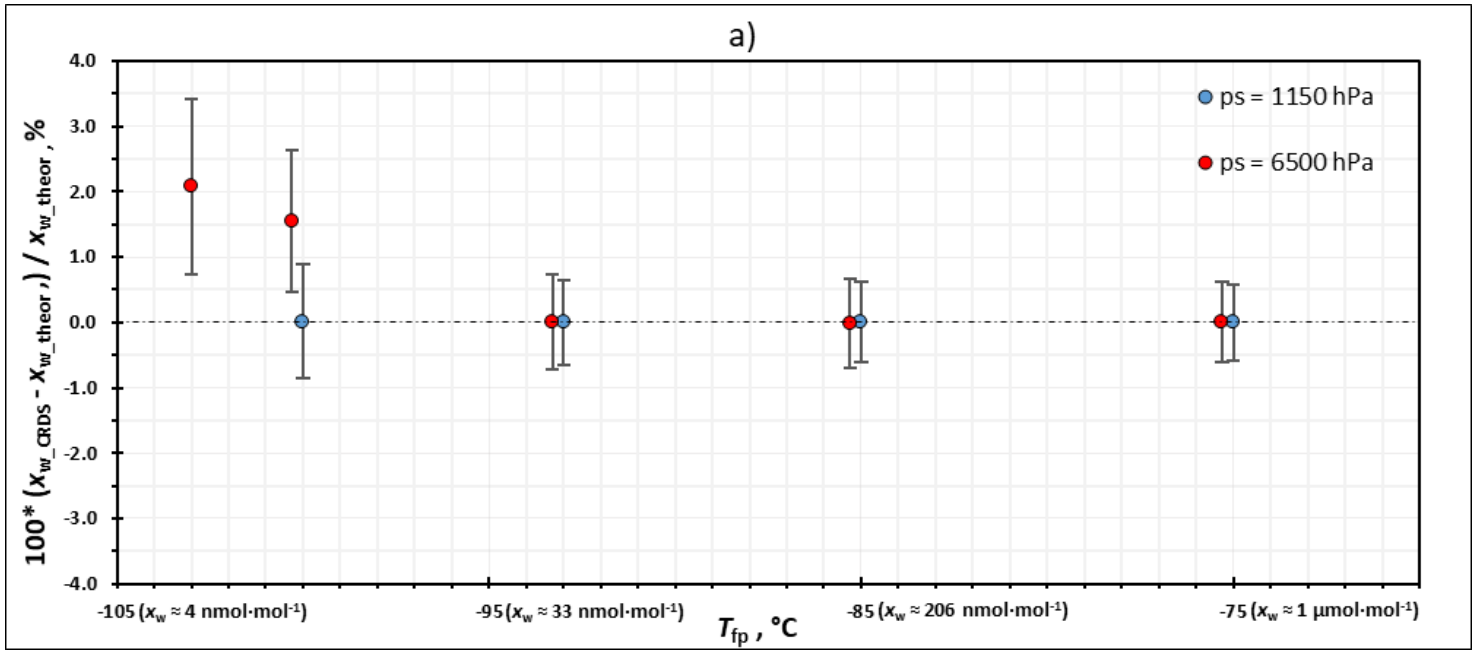


Response of the humidity generator at step changes of the saturator bath temperature (40 ppb to ppb).

- **red line**: water vapour amount fraction measured by a CRDS analyser;
- **black line**: reference water vapour amount fraction estimated from the measurement of T_{sat} and p_{sat}.



Percent difference between x_w as measured by a CRDS analyzer and the reference value in the range between 4 nmol mol^{-1} and 1000 nmol mol^{-1} in N_2

p_{sat} = 6500 hPa, T_{sat} = -97 °C, p_{out} = 1150 hPa

- T_{fp} = -105.10 °C $u_c(T_{fp})$ = 0.07 °C
- x_w = 4.2 nmol·mol^{-1} $u_c(x_w)$ = 60 pmol·mol^{-1} (1.4 %)

Saturation-based generators

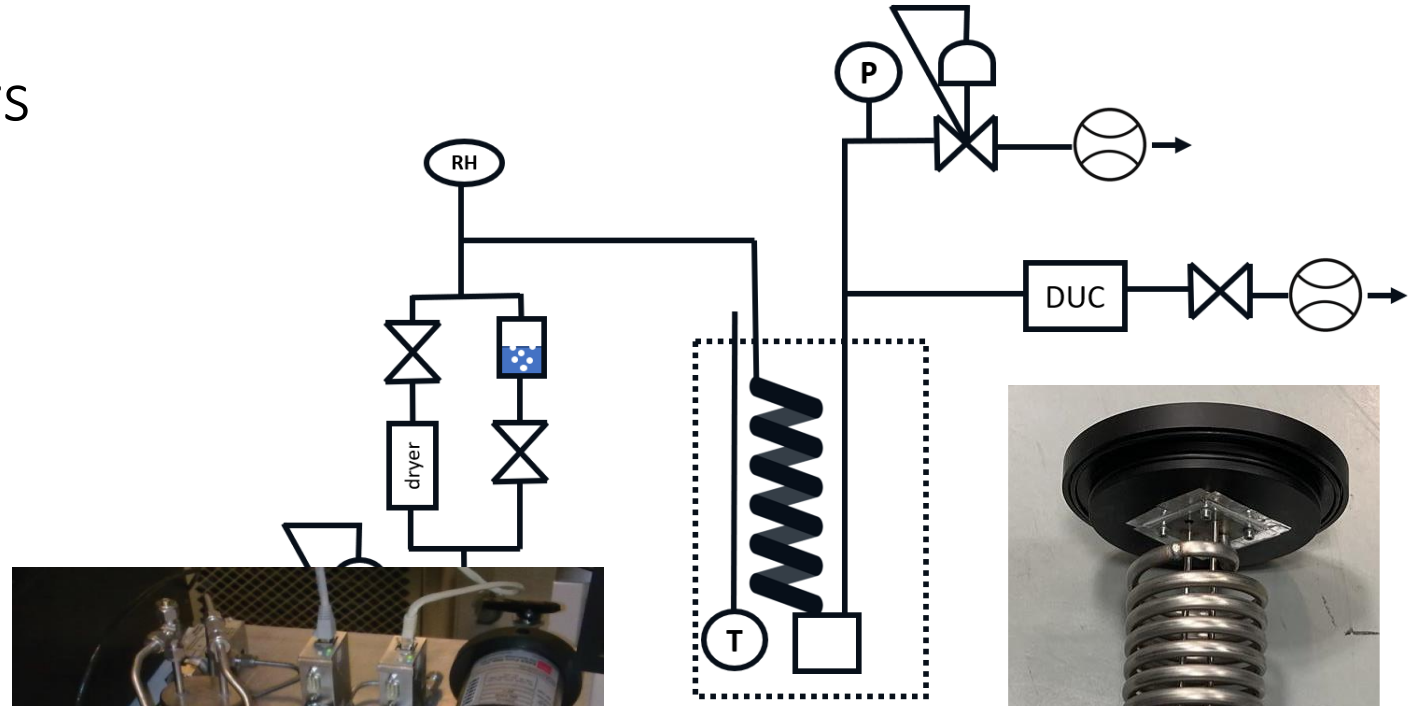
- Developed by **UL**, Slovenia
- frost-point down to -95 °C
  (expanded < -100 °C)
- pressure: up to **1 MPa** (CDA, N_2, Ar)
- uncertainty

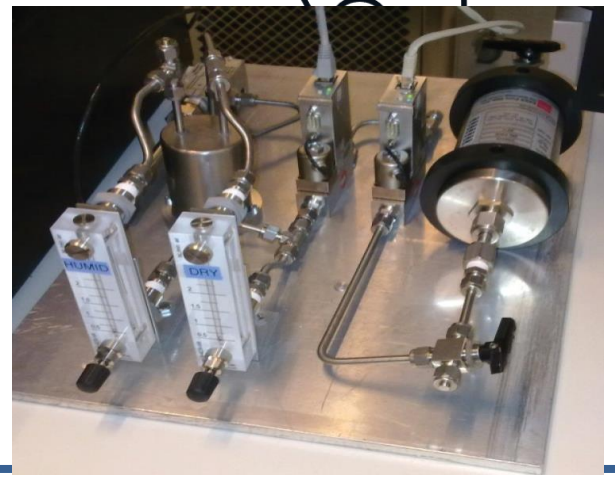
  $U(k=2)$ = 0,04 °C to 0,2 °C

Saturation-based generators

- Developed by VTT, Finland
- frost-point down to -100 °C
- a condenser instead of a saturator
- pressure: up to 0,7 MPa
- uncertainty @-100 °C & 0,1 MPa

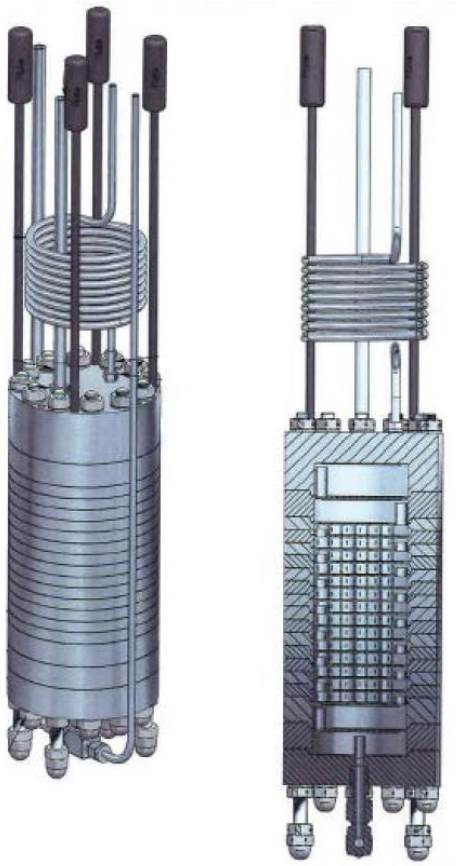
  $U(k=2)=0{,}08$ °C





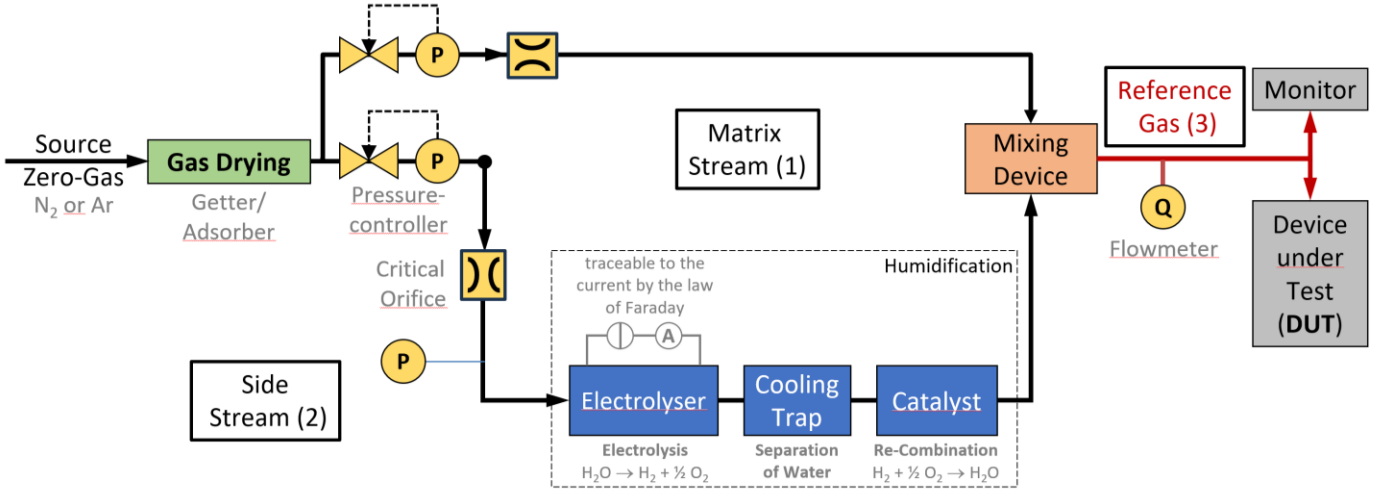
Saturation-based generators

- Developed by **INTA**, Spain
- Initial -75 °C, now -95 °C
- pressure: up to **0,5 MPa**
- new prototype – developed by **MBW** (for INTA): up to **40 MPa**



Coulometric Trace-Water Generator (CTWG)

- Developed by **PTB**, Germany
- Principle is based on electrolysis of water and catalytic recombination of produced hydrogen and oxygen
- Traceability of amount fraction to electrical current due to Faraday's law
- Target lower limit: **5 nmol/mol**
- Pressure: up to **0,14 MPa**



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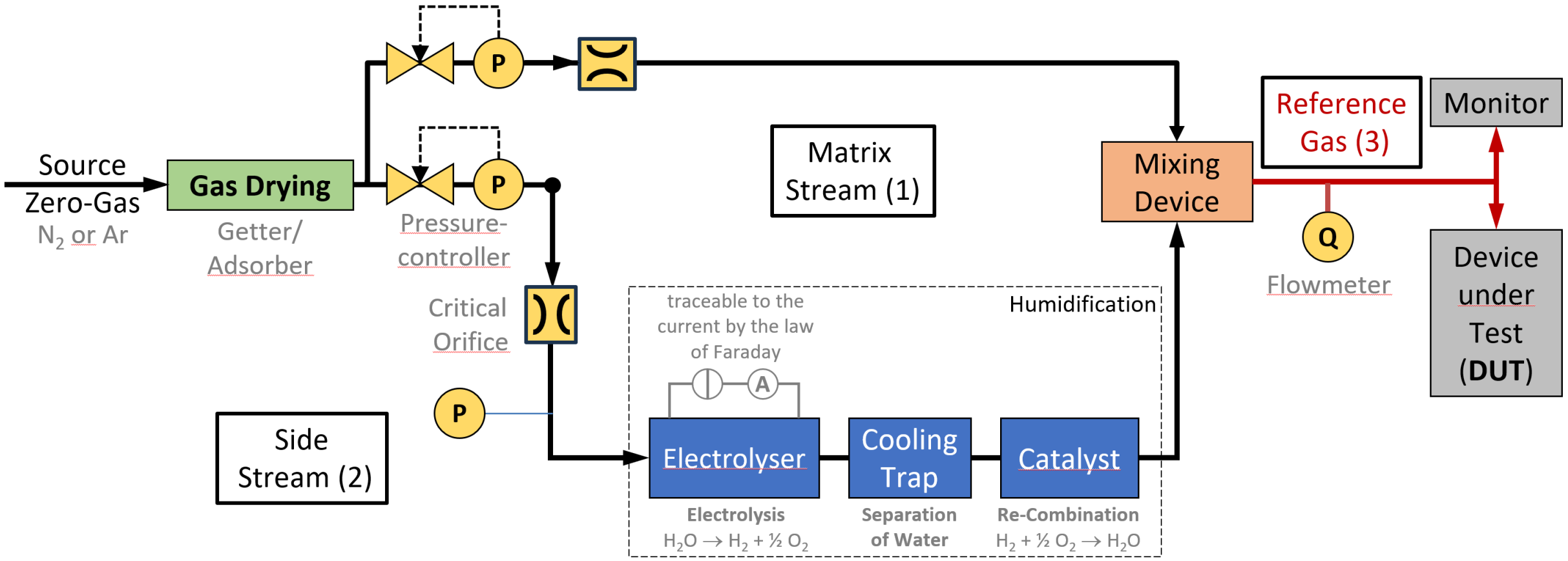

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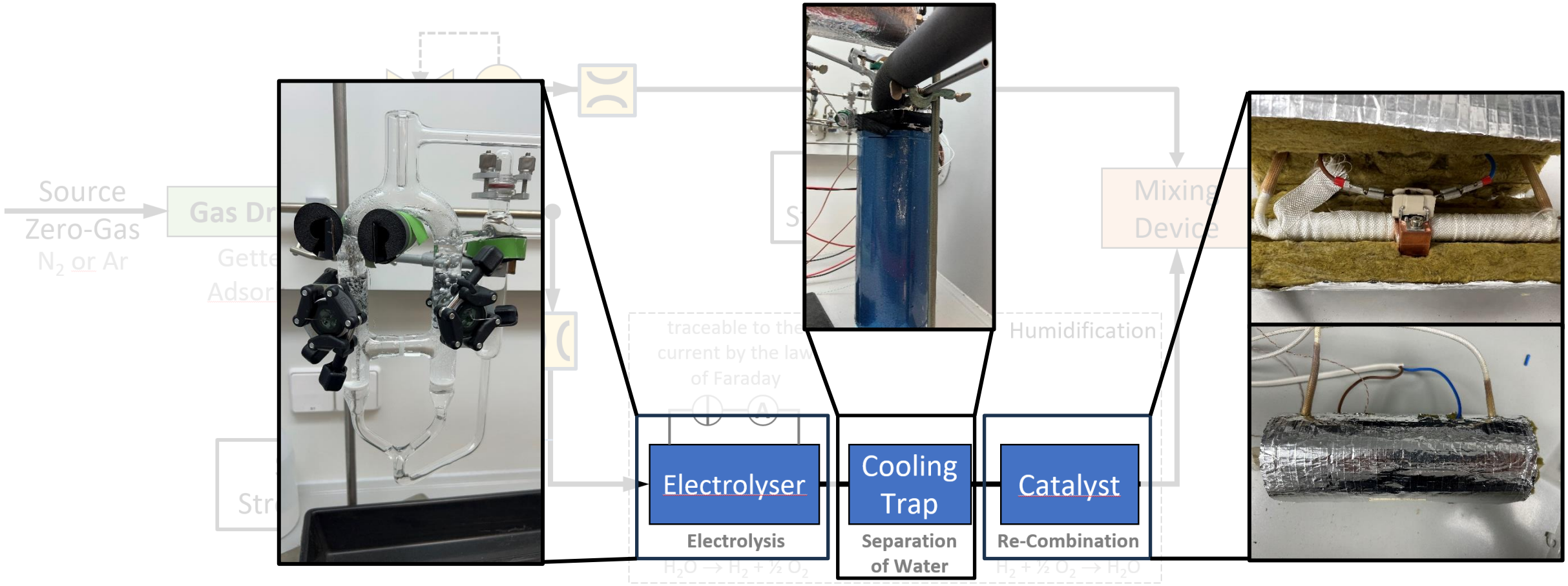
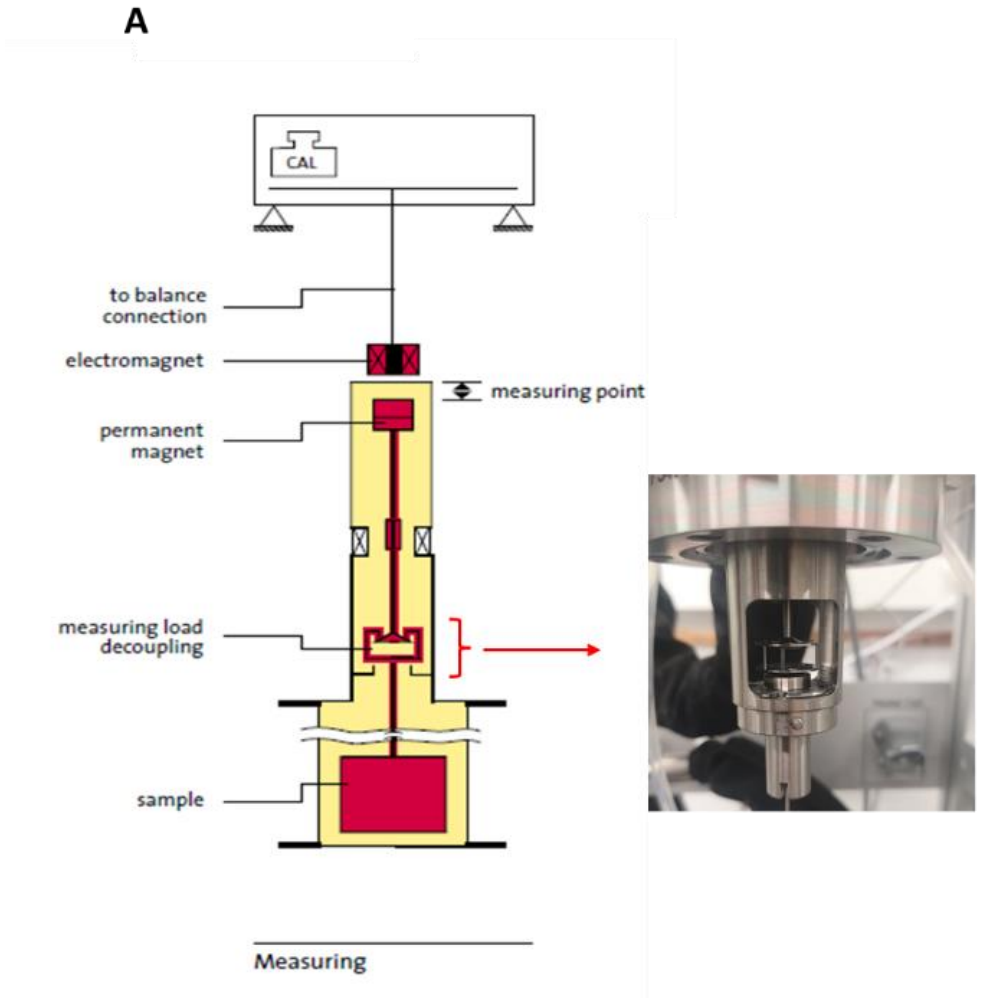


Permeation-based generators

- Developed by **VSL**, Netherlands
- Principle: Magnetic suspension balance – permeation rate is measured by weighing the mass decrease of the permeator through time
- well-suited for reactive analytes, such as NO2, SO2, NH3, organic compounds (VOC)



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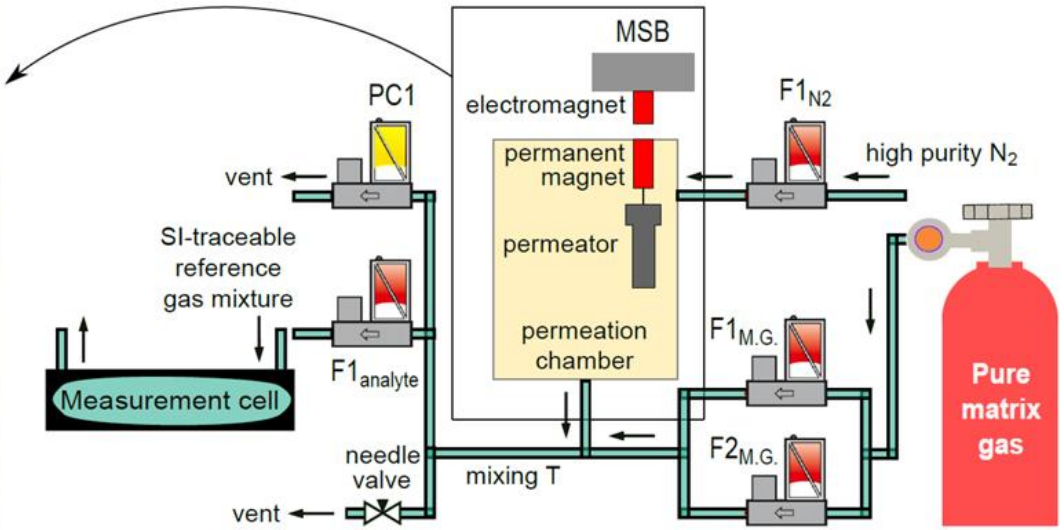

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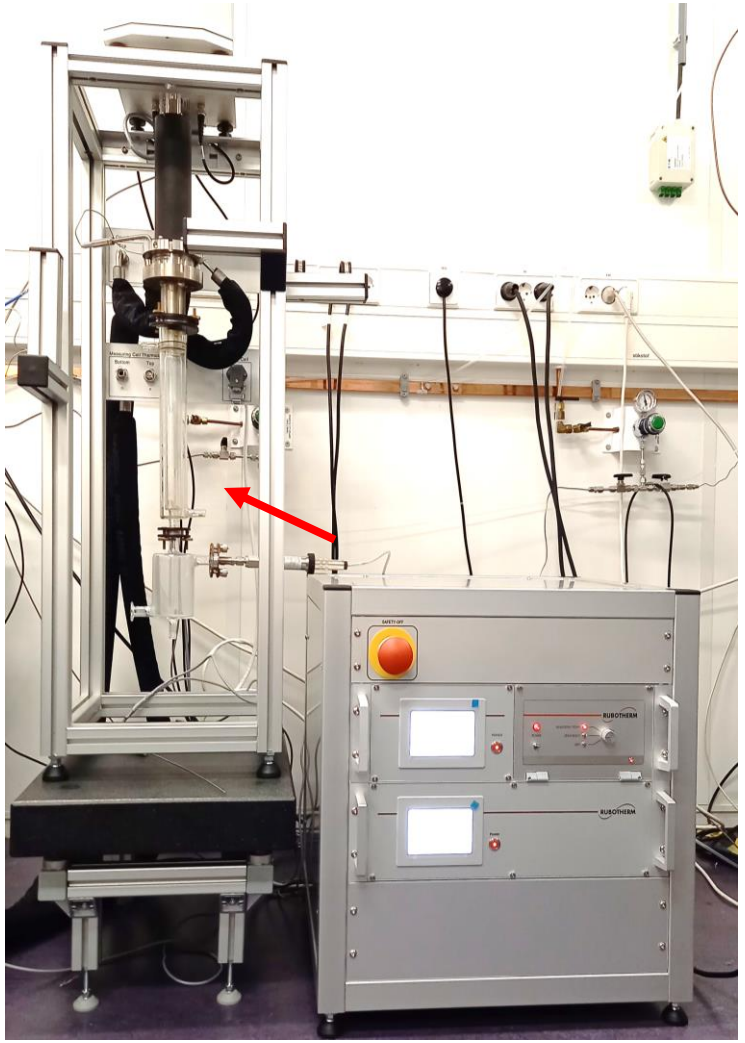

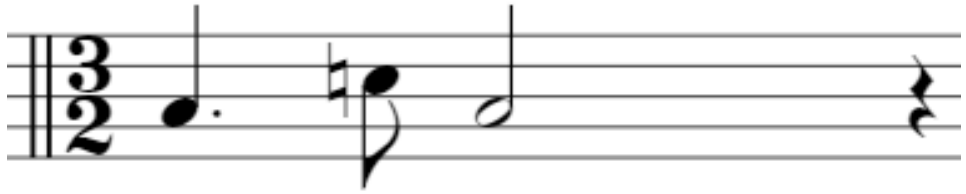

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