



VTT

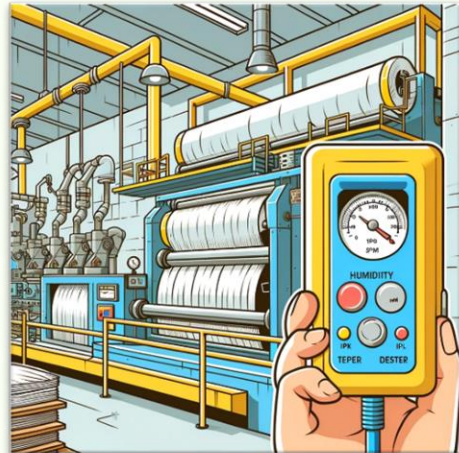
From Ideal to Real Gas Mixtures: What We Need to Know?

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15/05/2024

VTT – beyond the obvious

Non ideal mixtures: Who cares?



[Read more](#)





Under pressure?
You need some relief...

f

:Water Vapor Enhancement Factor

1. **UNICAS** performed an extensive literature review
2. **VTT** and **INRIM** employed numerical calculation models to generate large datasets and formulate functional equations.
3. **CNAM** and **CETIAT** Upgraded CNAM's microwave-based trace water analyzer to measure water vapor enhancement in nitrogen and argon across selected frost-point temperature and pressure ranges. **(dilution system + mwR)**
4. **CMI** Utilized an upgraded saturation-based generator to conduct independent measurements of water vapor enhancement in nitrogen and argon, evaluating the non-ideality of these gas mixtures. **(1P1T+CRDS)**
5. **VSL, UL** and **INRIM** performed the measurements of water vapor enhancement down to **-105 °C** in nitrogen and argon at various pressures using their existing standards. **(2P → f*)**
6. **PTB** confirmed the enhancement factor measurements using a coulometric-based generator
7. **Uva, INTA, CEM** Performed measurements to assess the enhancement of water vapor in nitrogen, argon, and hydrogen using improved equipment, contributing to a better understanding of gas mixture non-ideality. **(QSR+CMH)**
8. **VTT** validated and finetuned the water vapor enhancement factor functional equation coefficients based on the experimental data and uncertainty-aware data fusion techniques in a metrologically sound manner.
9. **UNICAS** launched the **PROMETH2O WebApp** to facilitate the end-user access to the functional equations

Water Vapor Enhancement Factor: Numerical Calculation Models

New experimental data for:

Nitrogen: $f.f^*$

Argon: $f.f^*$

Hydrogen: f



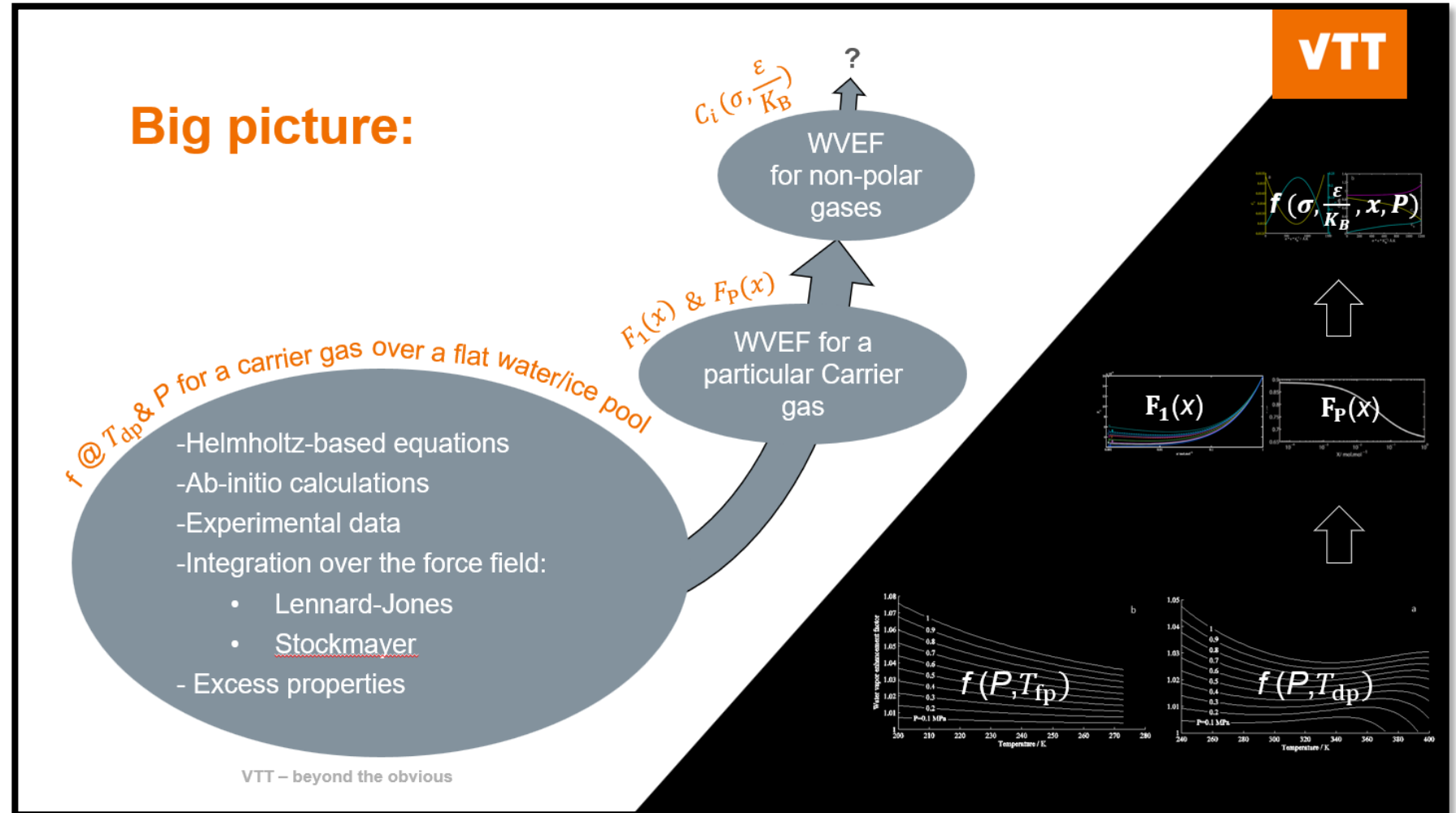
Validation of the calculations

Finetuning the numerical coefficients

Uncertainty estimation of the equations



Documentation and WebApp



$$f = \prod_{i=1}^{15} f_i,$$

$$f_1 = e^{[(1+K_T P_{ws})(p-P_{ws})-0.5K_T(P^2-P_{ws}^2)] \frac{\bar{v}_c}{RT}},$$

Eq.1.1

$$f_2 = 1 - \frac{x_a P}{K_a},$$

Eq.1.2

$$f_3 = e^{\frac{x_a^2 P}{RT} B_{aa}},$$

Eq.1.3

$$f_4 = e^{-2 \frac{x_a^2 P}{RT} B_{aw}},$$

Eq.1.4

$$f_5 = e^{-\frac{P-P_{ws}-x_a^2 P}{RT} B_{ww}},$$

Eq.1.5

$$f_6 = e^{\frac{x_a^3 P^2}{(RT)^2} C_{aaa}},$$

Eq.1.6

$$f_7 = e^{3 \frac{x_a^2 (1-2x_a) P^2}{2(RT)^2} C_{aaw}},$$

Eq.1.7

$$f_8 = e^{-3 \frac{x_a^2 (1-x_a) P^2}{(RT)^2} C_{aww}},$$

Eq.1.8

$$f_9 = e^{-\frac{(1+2x_a)(1-x_a)^2 P^2 - P_{ws}^2}{2(RT)^2} C_{www}},$$

Eq.1.9

$$f_{10} = e^{-\frac{x_a^2 (1-3x_a)(1-x_a) P^2}{(RT)^2} B_{aa} B_{ww}},$$

Eq.1.10

$$f_{11} = e^{-2x_a^3 \frac{(2-3x_a) P^2}{(RT)^2} B_{aa} B_{aw}},$$

Eq.1.11

$$f_{12} = e^{6x_a^2 \frac{(1-x_a)^2 P^2}{(RT)^2} B_{aw} B_{ww}},$$

Eq.1.12

$$f_{13} = e^{-\frac{3x_a^4 P^2}{2(RT)^2} B_{aa}^2},$$

Eq.1.13

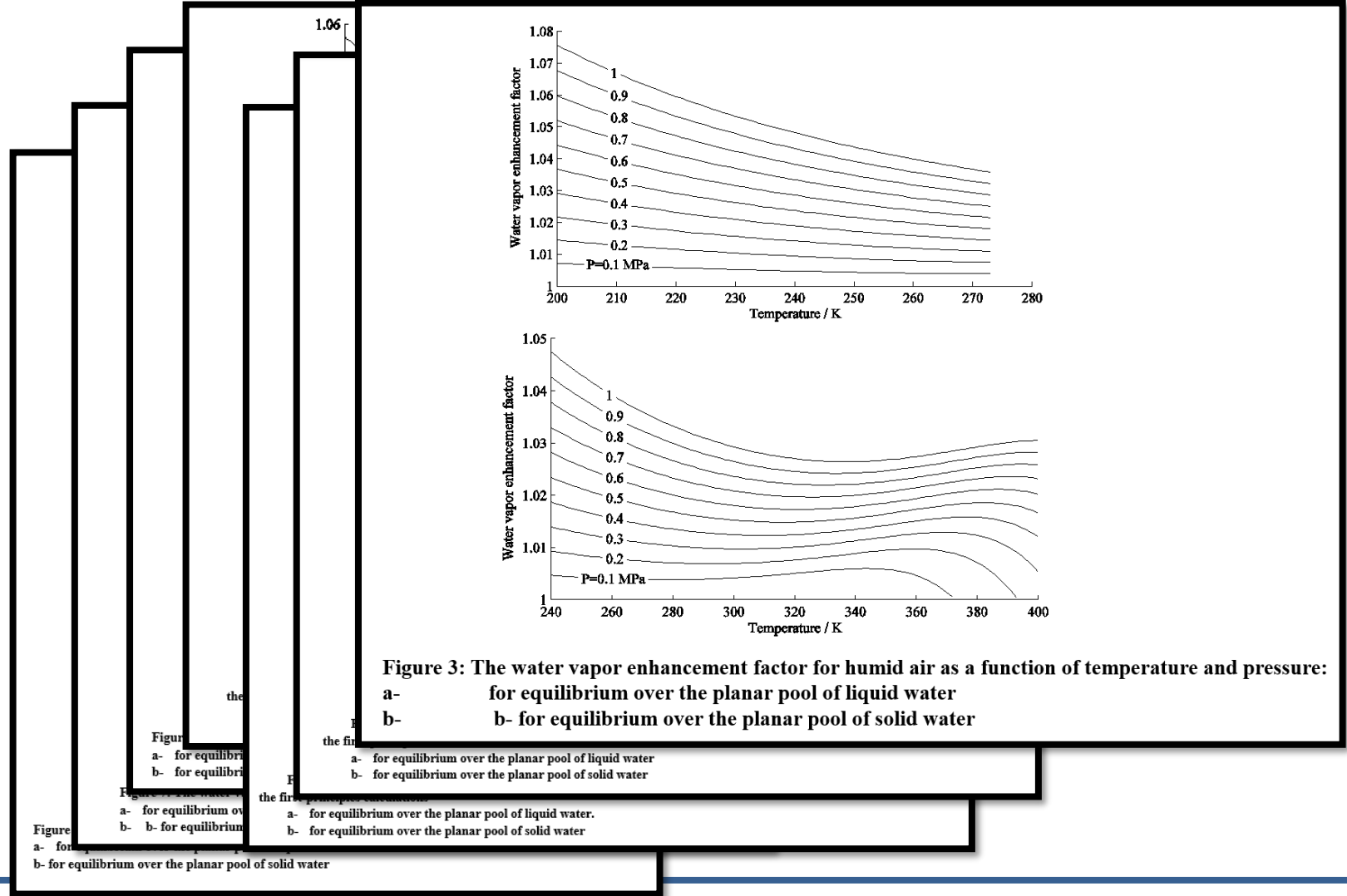
$$f_{14} = e^{-2x_a^2 \frac{(1-x_a)(1-3x_a) P^2}{(RT)^2} B_{aw}^2},$$

Eq.1.14

$$f_{15} = e^{-\frac{P_{ws}^2 - (1+3x_a)(1-x_a)^3 P^2}{2(RT)^2} B_{ww}^2},$$

Eq.1.15

air	Experimental
air	Ab-initio calculations
nitrogen	LJ potential
nitrogen	Ab-initio calculations
argon	LJ potential
argon	Ab-initio calculations
methane	LJ potential
hydrogen	LJ potential
Oxygen	LJ potential
Oxygen	Ab-initio calculations
CO2	LJ potential



$$\left(f_{\rho}^{AV} + f_{q\rho}^{AV} - \frac{P}{(\rho^{AV})^2} \right) \Delta\rho^{AV} - \left(f_{\rho}^{W} - \frac{P}{(\rho^W)^2} \right) \Delta\rho^W =$$

$$P \left(\frac{1}{\rho^W} - \frac{1}{\rho^{AV}} \right) + f^W \cdot f^{AV} + (q - 1) f_q^{AV},$$

$$(2f_{\rho}^{AV} + \rho^{AV} f_{\rho\rho}^{AV}) \Delta\rho^{AV} = \frac{P}{\rho^{AV}} - \rho^{AV} f_{\rho}^{AV},$$

$$(2f_{\rho}^W + \rho^W f_{\rho\rho}^W) \Delta\rho^W = \frac{P}{\rho^W} - \rho^W f_{\rho}^W.$$

$$f(P, T_{dP}) = \frac{xP}{P_{ws}(T_{dP})},$$

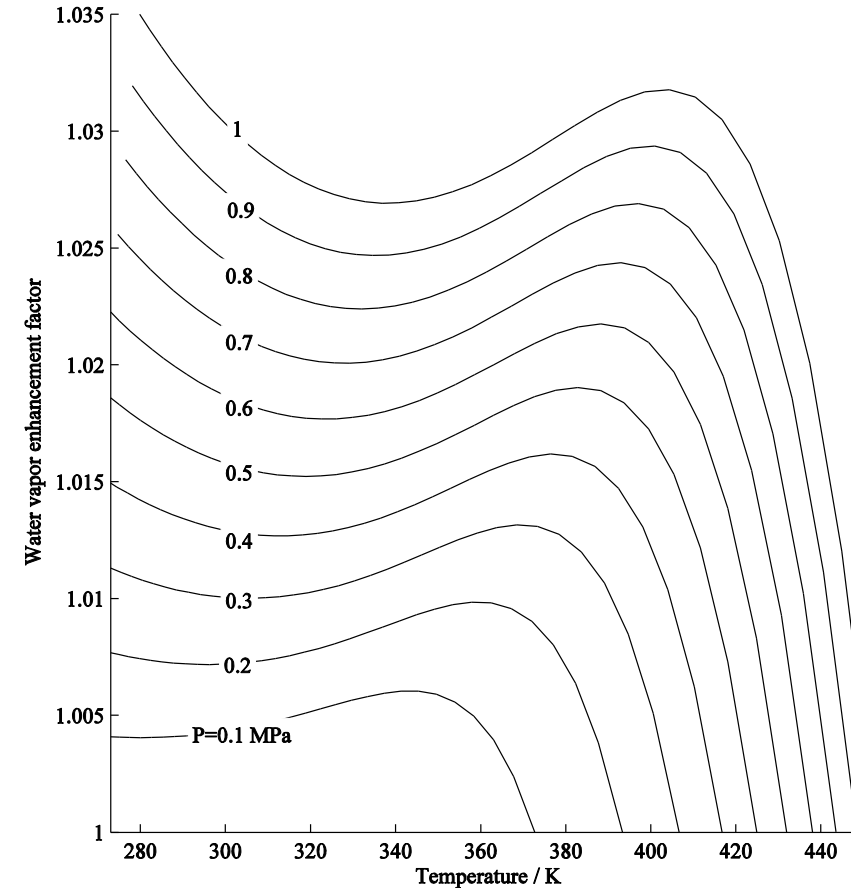


Figure 4: The water vapor enhancement factor for equilibrium over a planar pool of liquid water based on the second method

$$f = e^{(1-x)F_1(x)P^{F_P(x)}}, \quad \text{Eq.16}$$

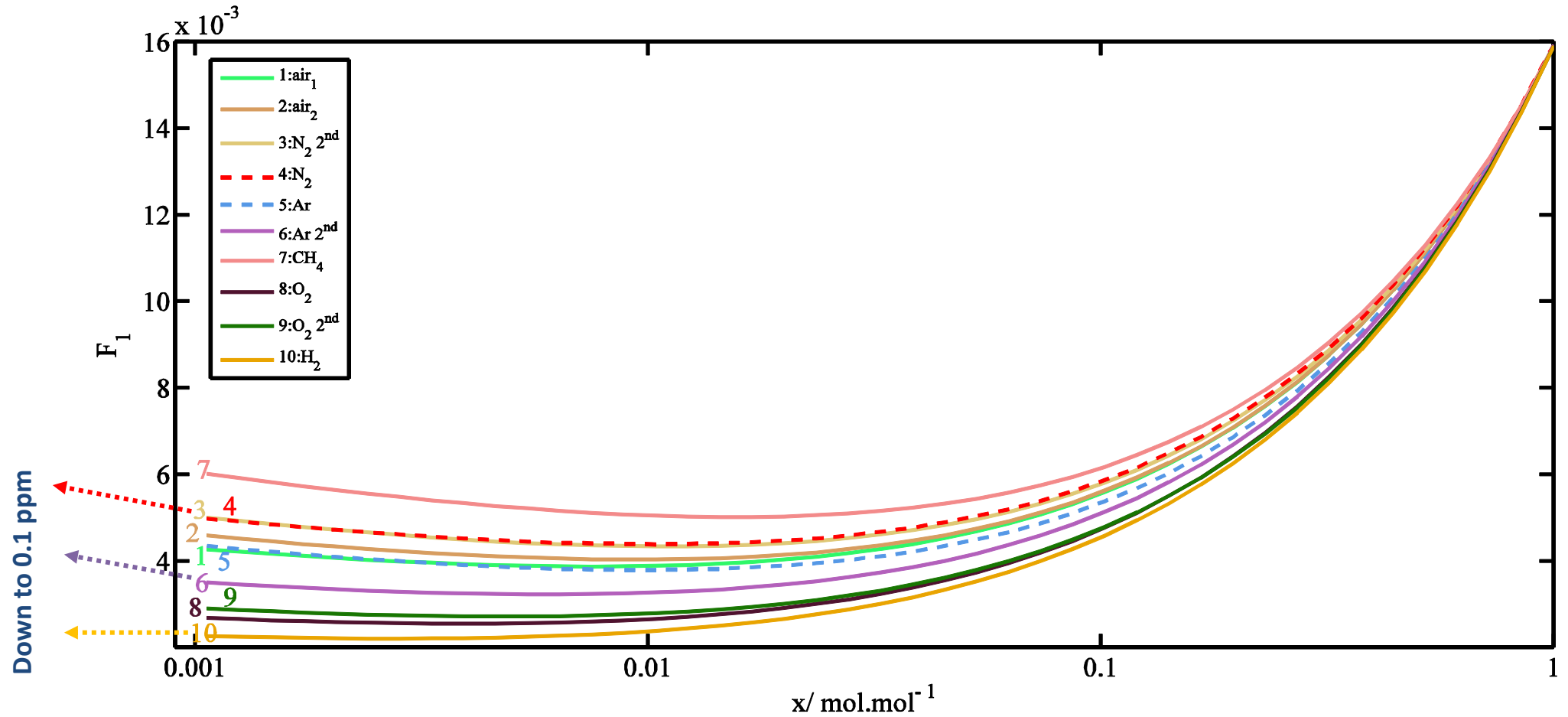
$$F_1(x) = C_1[(x^{0.67} - 1) + C_2 \cdot (x^{-0.1} - 1)] + 0.0158, \quad \text{Eq.17}$$

$$F_P(x) = F_{P,d} + \bar{a}[\tanh(\bar{b} \cdot \ln(x) + \bar{c}) + 1] \approx F_{P,d} + \frac{-0.1963 \cdot x^{c_3}}{c_3 \cdot (x^{c_3} + c_4)}. \quad \text{Eq.18}$$

The **universal** values are best estimated to be $F_{p,d} = 0.888$ $C_3 = 0.8429$ $C_4 = 0.0663$

$$F_{1,ice} = (1.091 + 0.01431 \cdot \ln(x)) \cdot F_{1,water}, \quad \text{Eq.19}$$

$$F_{p,ice} = F_{p,water} + 0.0175. \quad \text{Eq.20}$$



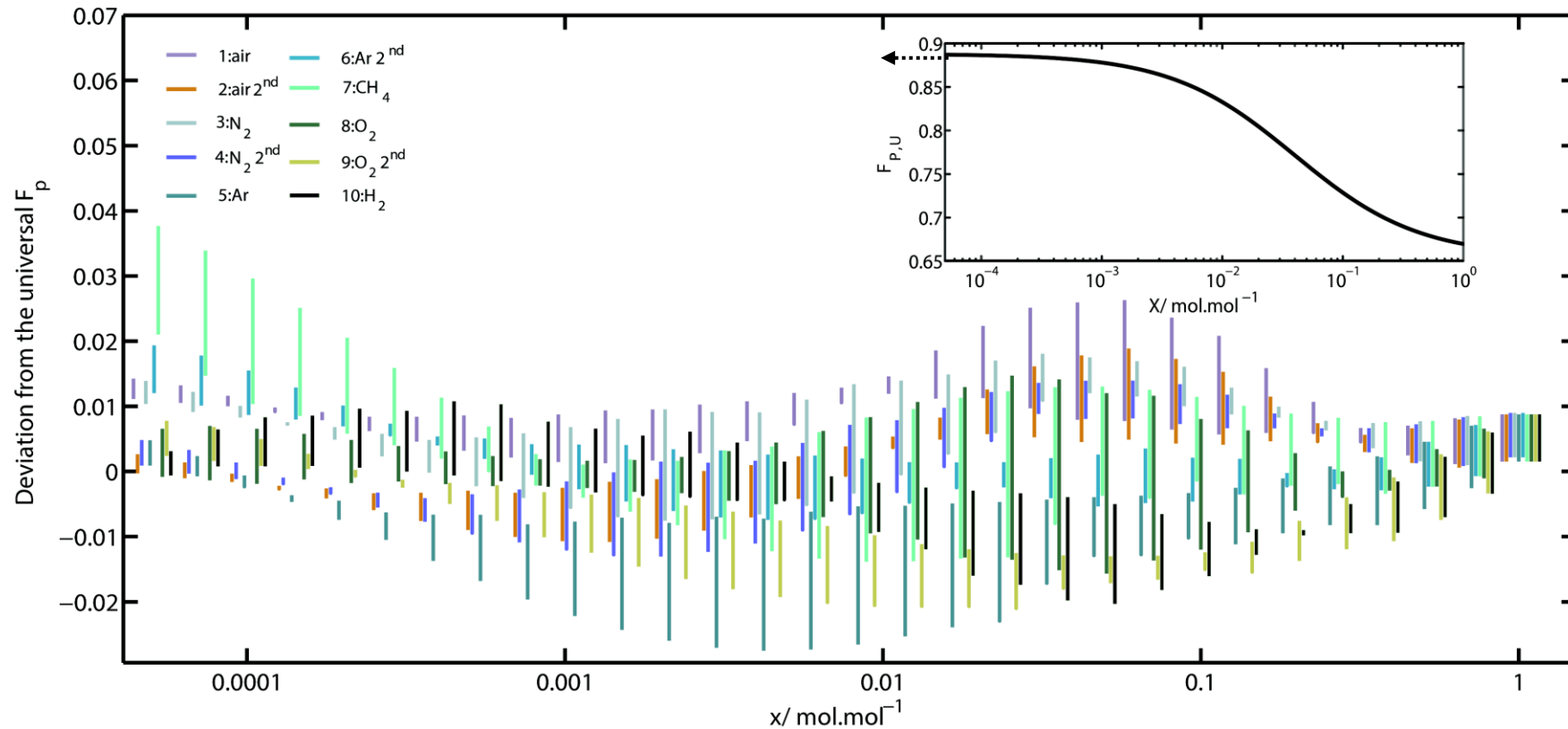
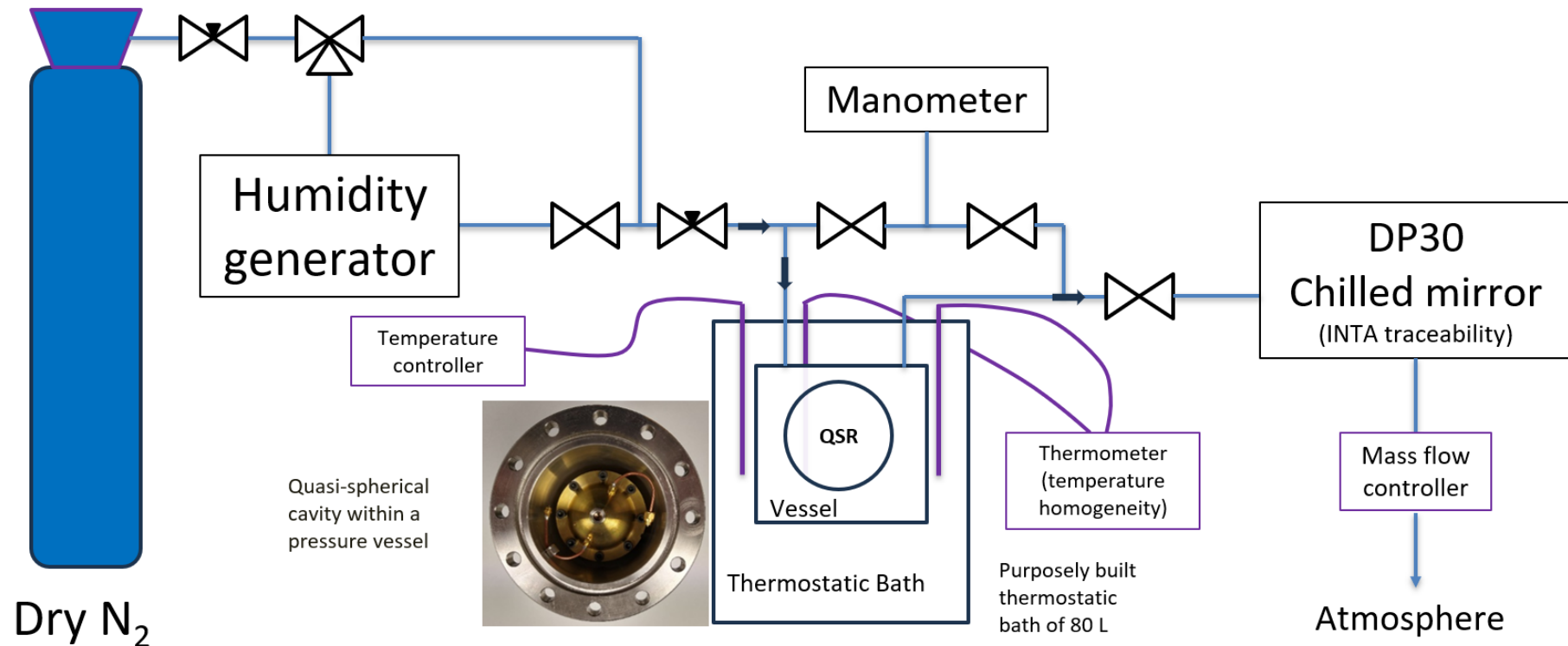


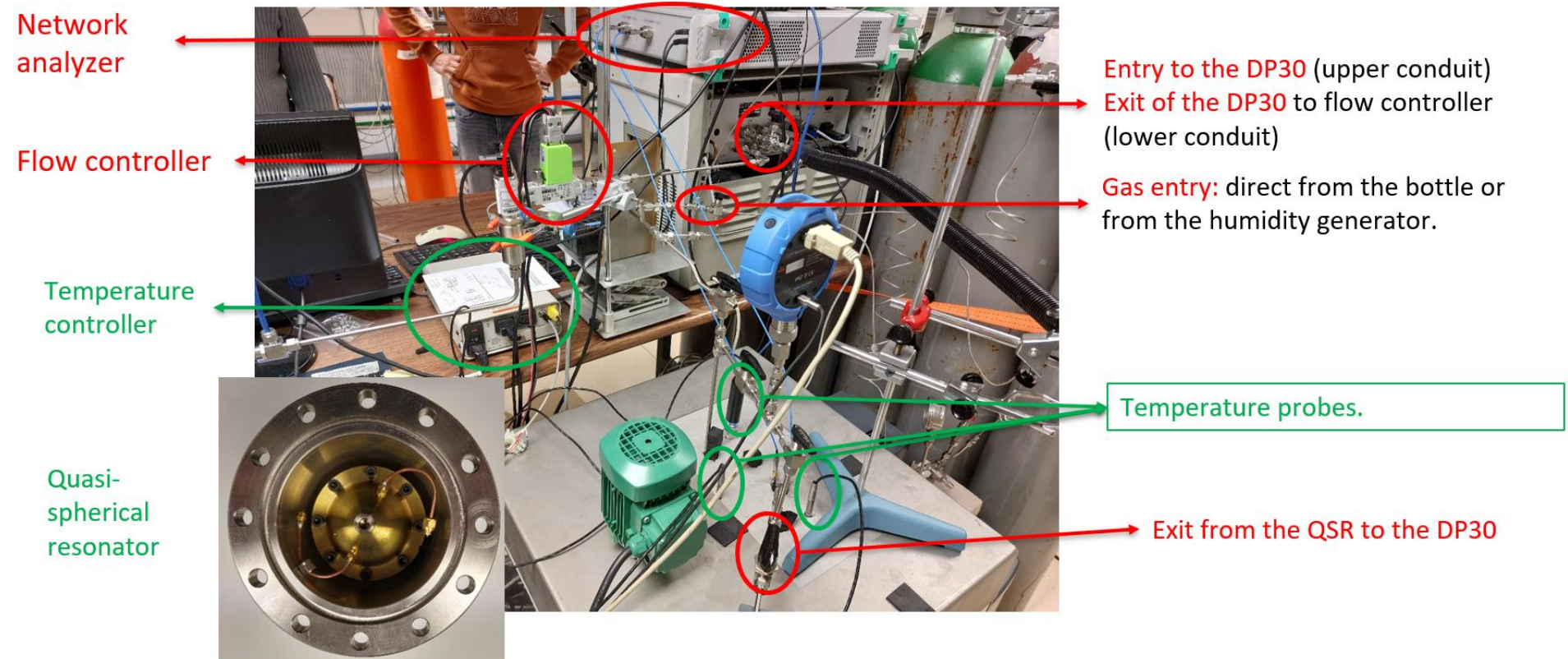
Figure 16: The pressure factor. F_P . for various carrier gasses. bars are indicative of the pressure dependence; uncertainty levels are way bigger. Bars are moved horizontally for the sake of visualization.

Water Vapor Enhancement Factor: Experimental Setups



Pressure Control upstream: micrometric needle valves, the pressure regulator at the bottle.

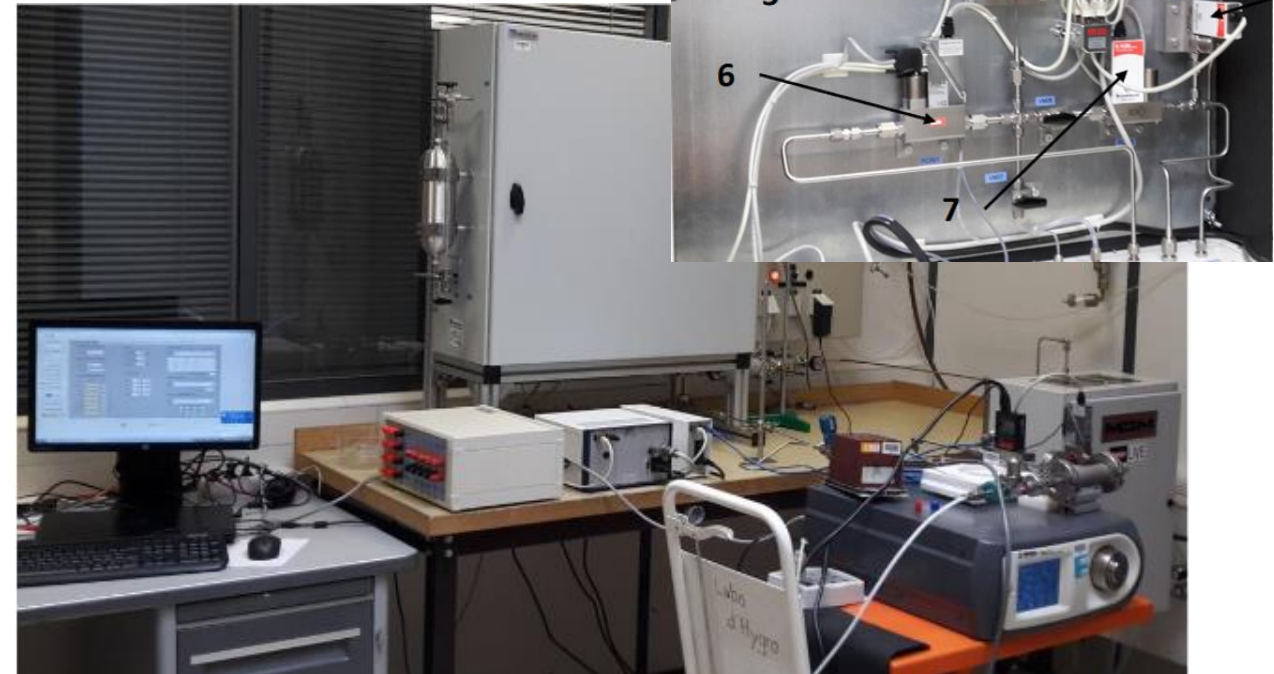




The measurement setup consists of the quasi-spherical cavity within a pressure vessel immersed in a purposely built thermostatic bath of 80 L. Inside the bath, there are three temperature probes, one used to control and maintain the temperature at the desired setpoint, and the other two to check for homogeneity. A calibrated manometer is located at the exit of the resonator. The humid gas mixture flows downstream to a DP30 hygrometer lent by INTA with traceability provided by them. At the exit of the DP30 hygrometer, we use a flow controller to obtain the desired flow. Several valves, along with the pressure regulator at the bottle, are used to control the pressure before entering the resonator.

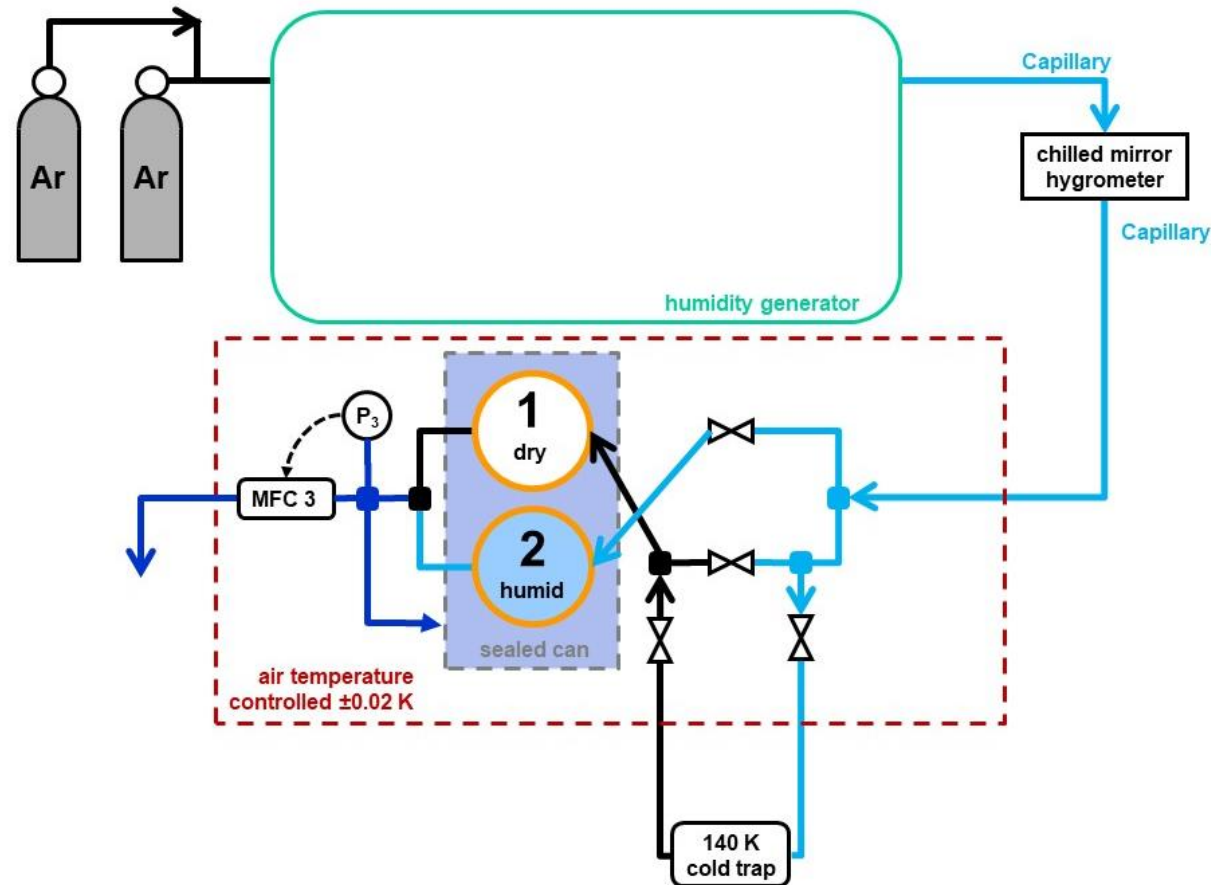
CETIAT upgraded the Mixed Flow Humidity Generator (MFHG) for this project enhancing its capability to handle:

- Pressure: 1 bar to 10 bar
- Carrier gases: Air, Nitrogen, and Argon
- Frost-point temperature: -80 °C to -30 °C

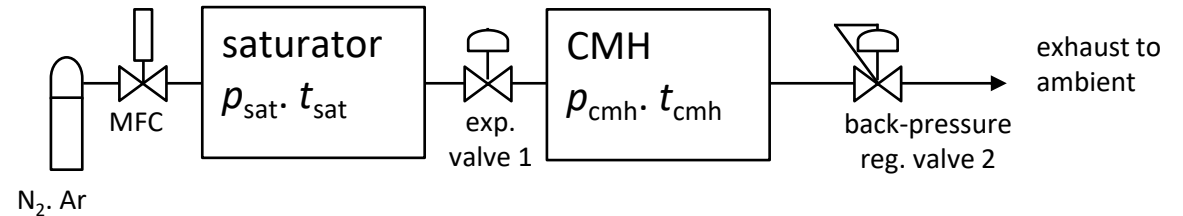
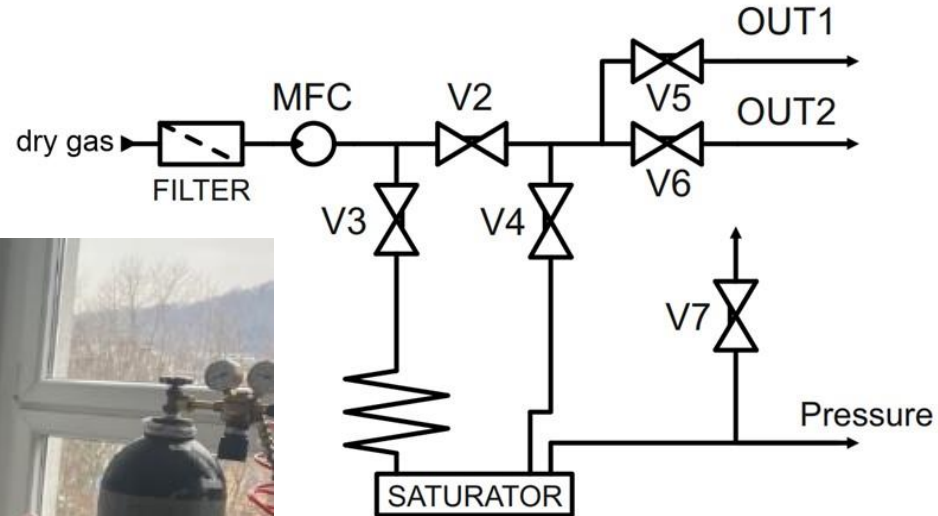


- two quasi-spherical copper resonators of 2.5 cm of ray. covered with a layer of gold
- the resonant frequency of the resonator depends on temperature. pressure. and composition of the gas inside. If pressure and temperature are known and stabilised. the resonance frequency depends only on the composition of the gas.
- by measuring the resonant frequency of the same gas with and without humidity. the difference should attenuate the effects of the environment.
- the inlet humid gas is divided in 2: half steam passes through a liquid N₂ cooled cold trap at 140 K that removes all the molecules of water. The dry gas enters resonator 1. The humid gas passes through resonator 2. and then the two steams are recombined.

- at the outlet. the pressure is measured and stabilised.
- the temperature of the spheres is measured using four pt100 temperature sensors in series on each sphere. Resonance frequencies and measured with lock-in amplifiers. The sealed can is connected to the outlet pressure.

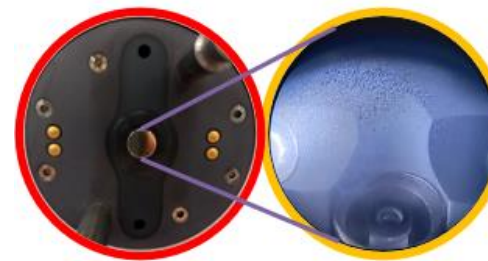
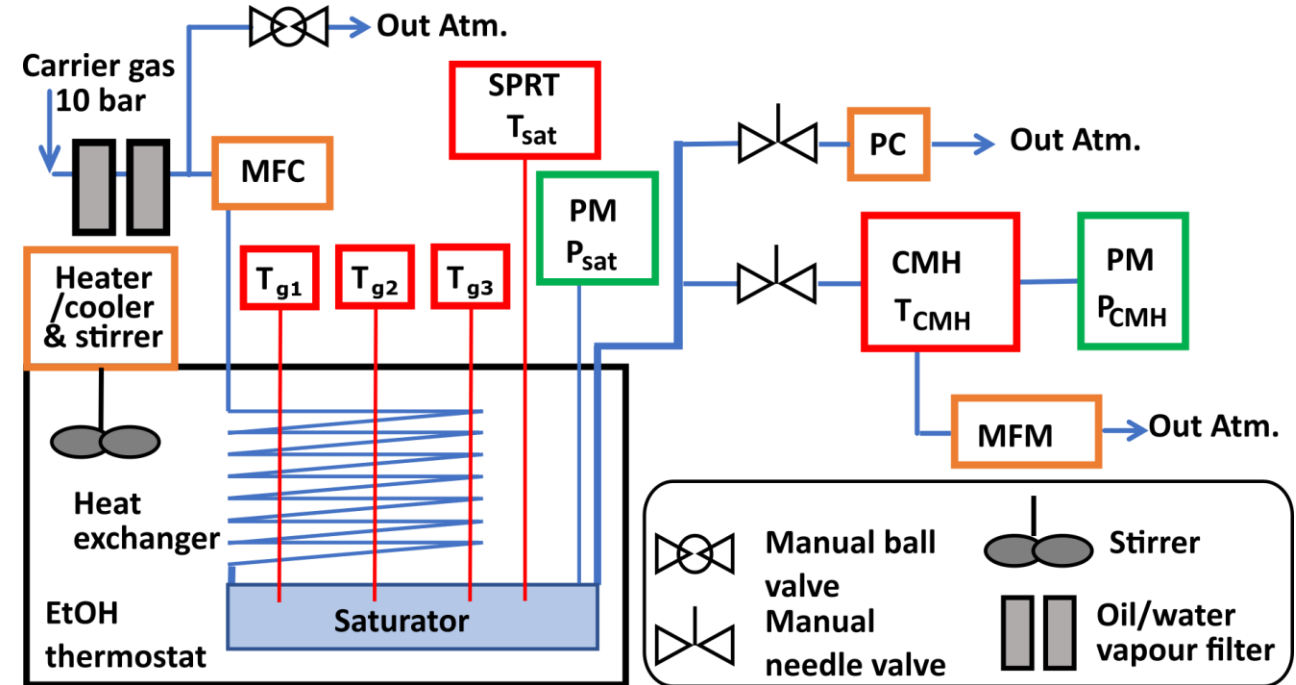
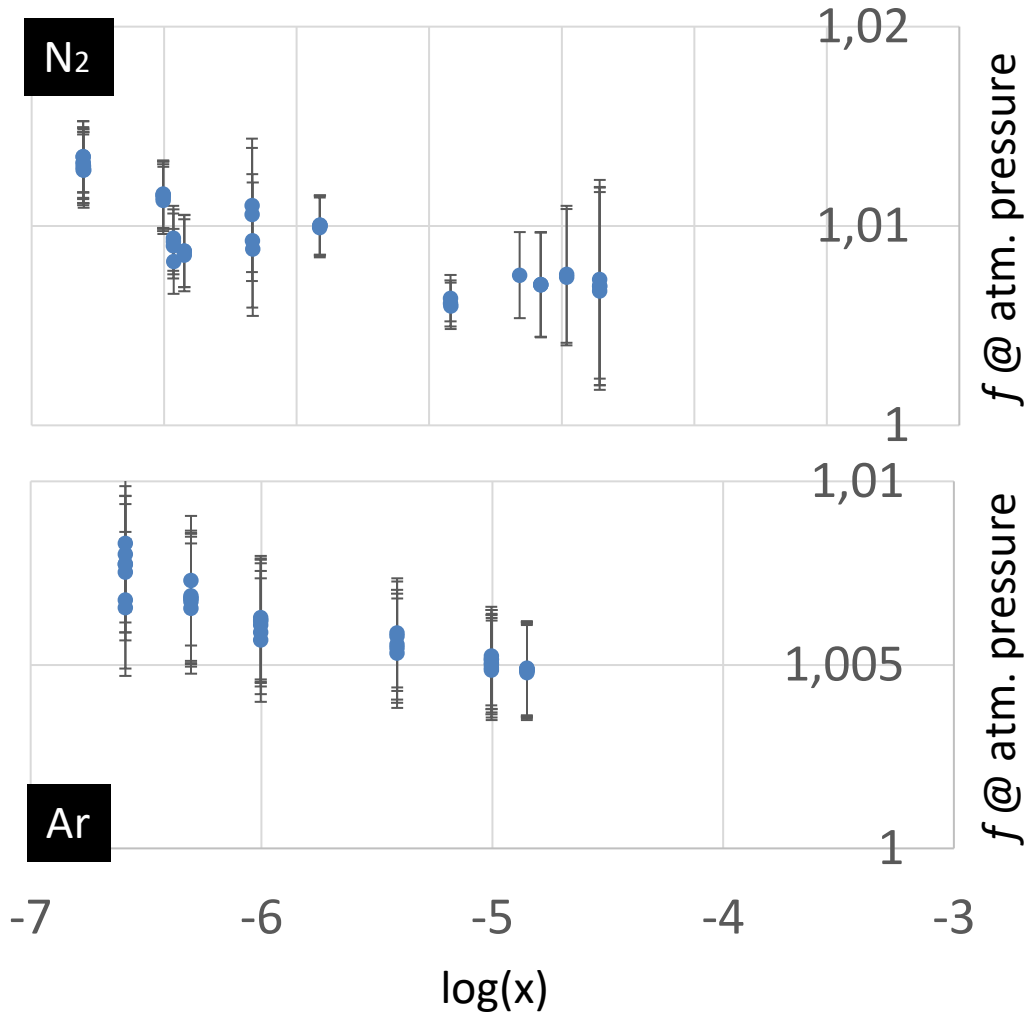


$$f' = \frac{f(t_{\text{sat}} \cdot p_{\text{sat}})}{f(t_{\text{cmh}} \cdot p_{\text{cmh}})} = \frac{e_s(t_{\text{cmh}})}{e_s(t_{\text{sat}})} \cdot \frac{p_{\text{sat}}}{p_{\text{cmh}}}$$



Example of the results @ -30 °C. 10 bar:

$f^* = 1.0435$	vs.	1.0451	(N2 ab-initio)
		1.045	(N2 PROMETH2O)
		1.0396	(Greenspan)



Chilled Mirror Hygrometer (CMH)
MBW 373 LX



Saturator (sat)

$$f_{\text{measured}}^* = \frac{e(T_{d.\text{measured}}^{\text{CMH}})_{\text{formula}}}{e(T_{d.\text{measured}}^{\text{sat}})_{\text{formula}}} \cdot \frac{p_{\text{measured}}^{\text{sat}}}{p_{\text{measured}}^{\text{CMH}}} = \frac{e(T_d^{\text{CMH}} + \delta T_d^{\text{CMH}}) + \delta e(T_d^{\text{CMH}})}{e(T_d^{\text{sat}} + \delta T_d^{\text{sat}}) + \delta e(T_d^{\text{sat}})} \cdot \frac{p_{\text{sat}} + \delta p_{\text{sat}}}{p_{\text{CMH}} + \delta p_{\text{CMH}}}$$

T_d^{sat}
$\delta T_{\text{sat. cal}}^s$
$\delta T_{\text{sat. drift}}^s$
$\delta T_{\text{sat. self-heat}}^s$
$\delta R_{\text{s.cal}}^s$
$\delta W_{\text{bridge. Cal}}^s$
$\delta W_{\text{bridge. resolution}}^{r_m}$
$\delta T_{\text{sat. stability}}^{r_m}$
$\delta T_{\text{gradient}}^{r_m}$
δT_d^{sat}

T_d^{CMH}
$\delta T_{\text{efficiency}}^s$
$\delta T_{\text{contamination}}^{r_m}$
$\delta T_{\text{CMH. stability}}^{r_m}$
$\delta T_{\text{CMH. resolution}}^{r_m}$
$\delta T_{\text{CMH. flow}}^{r_m}$
δT_{fit}
$\delta \Delta P_{\text{CMH}}^s$
$\delta \Delta P_{\text{sat}}^s$
δT_d^{CMH}

$e(T_d^{\text{sat}})$
$\delta T_{\text{formula}}^{\text{sat}}$
$e(T_d^{\text{CMH}})$
$\delta T_{\text{formula}}^{\text{CMH}}$

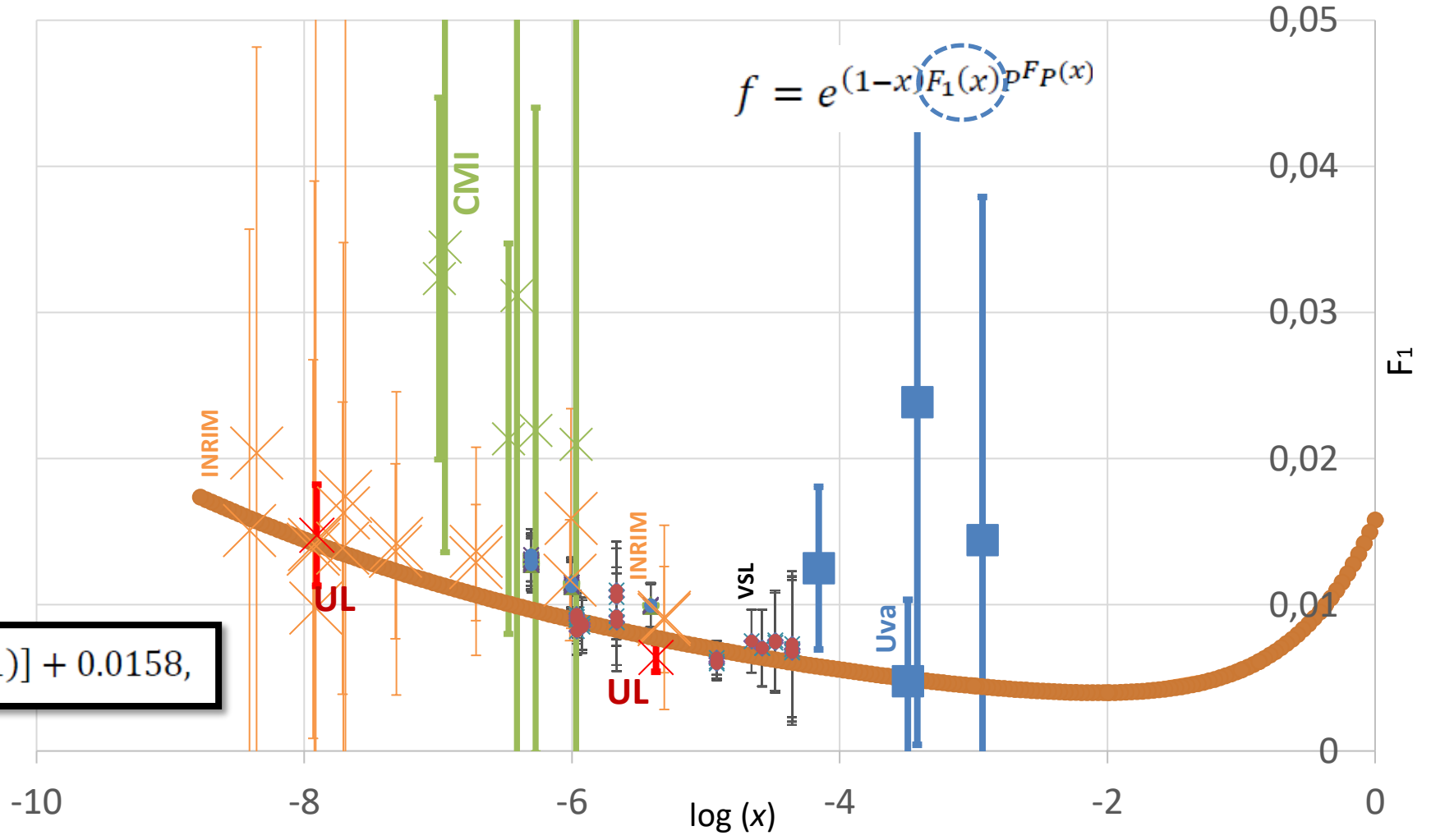
$p_{\text{measured}}^{\text{sat}}$
δP_{sat}^s
$p_{\text{measured}}^{\text{CMH}}$
δP_{CMH}^s

- T_CMH
- T_SAT
- P_CMH
- P_SAT
- e_CMH
- e_SAT



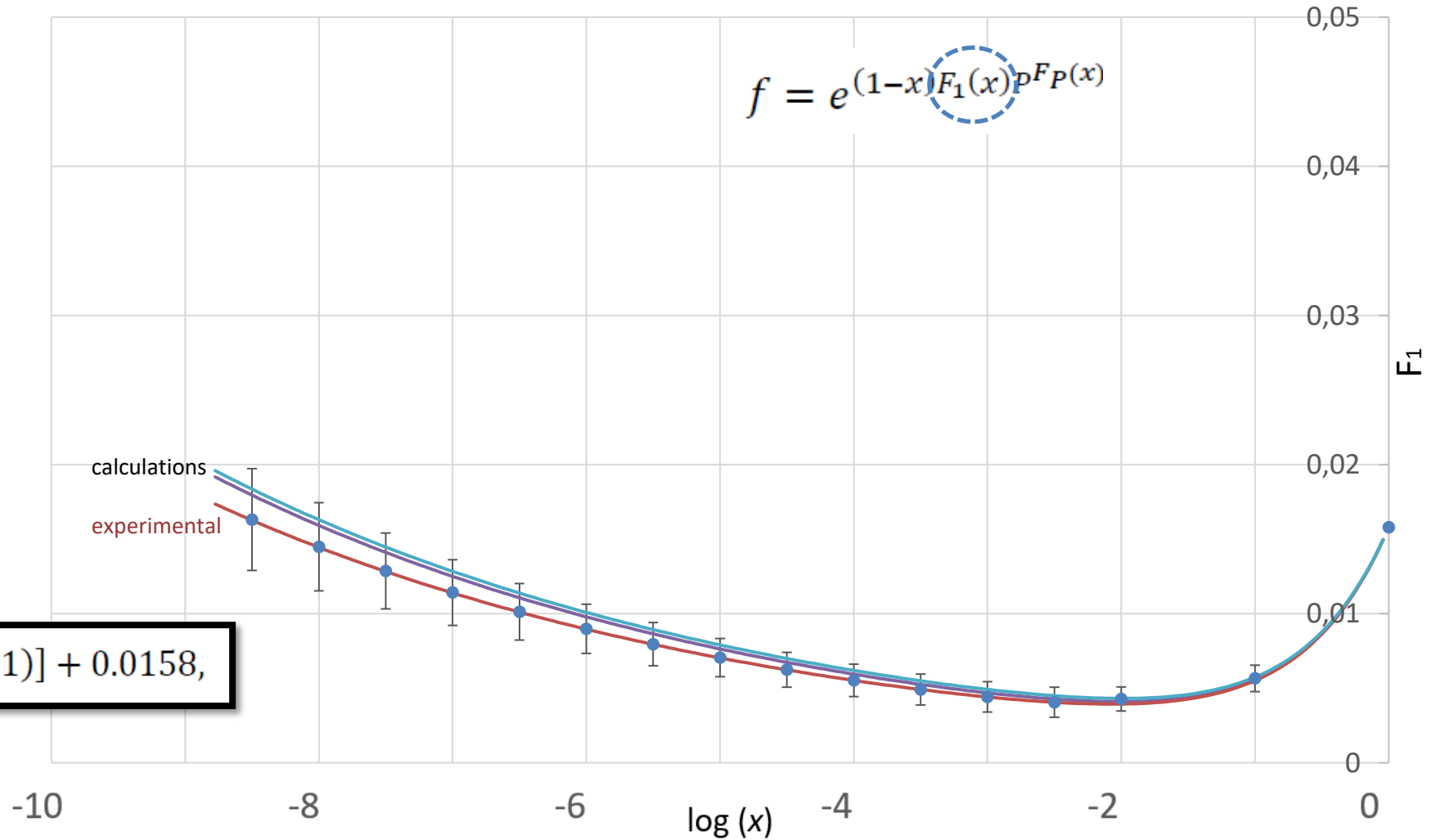
Provisional coefficients	
N2	
C ₁	0,013869
u(c ₁)	6E-04
C ₂	0.170
u(c ₂)	0.02

$$F_1(x) = C_1[(x^{0.67} - 1) + C_2 \cdot (x^{-0.1} - 1)] + 0.0158,$$



Provisional coefficients	
N2	
C1	0,013869
u(c1)	6E-04
C2	0.170
u(c2)	0.02

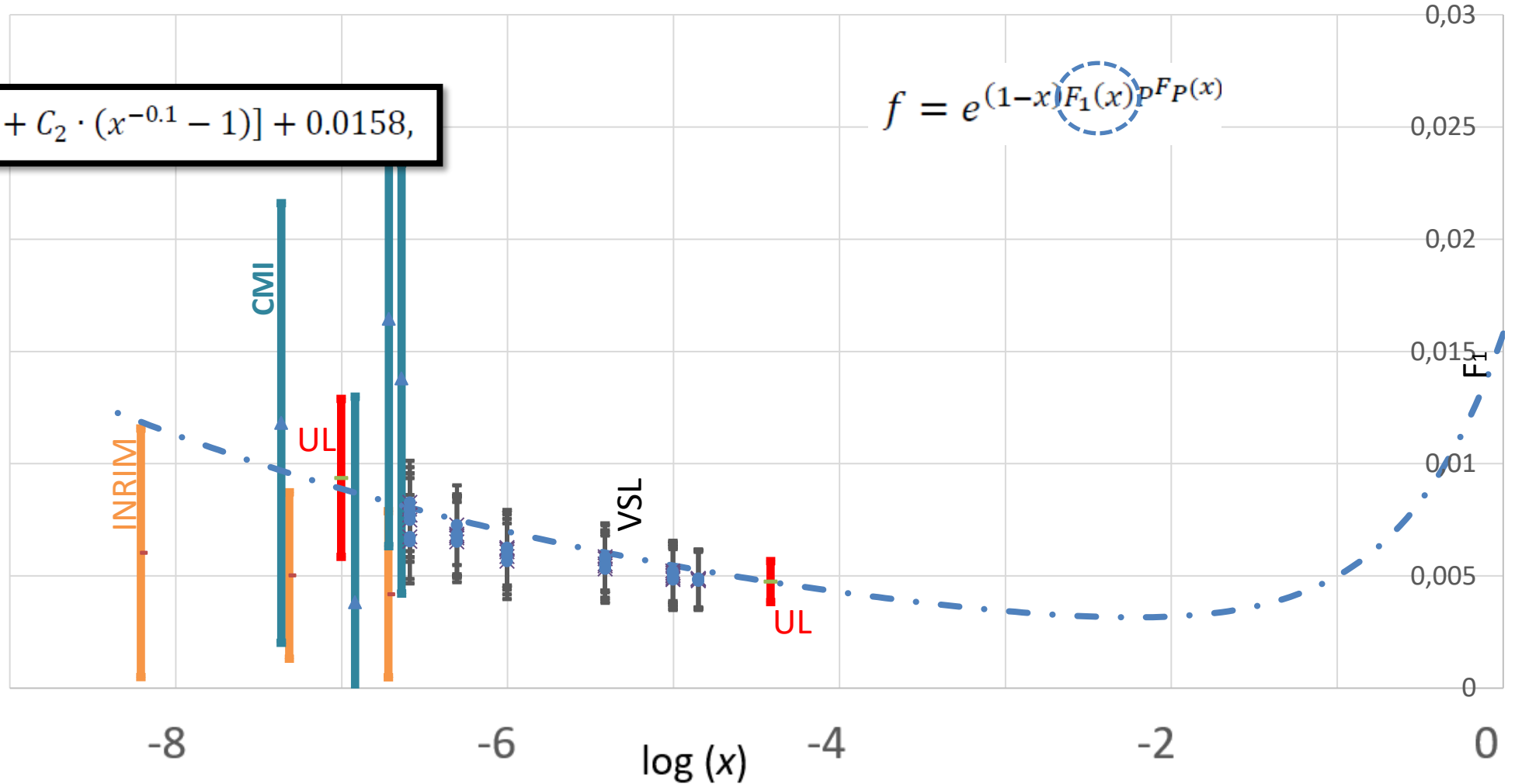
$$F_1(x) = C_1[(x^{0.67} - 1) + C_2 \cdot (x^{-0.1} - 1)] + 0.0158,$$



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Provisional coefficients

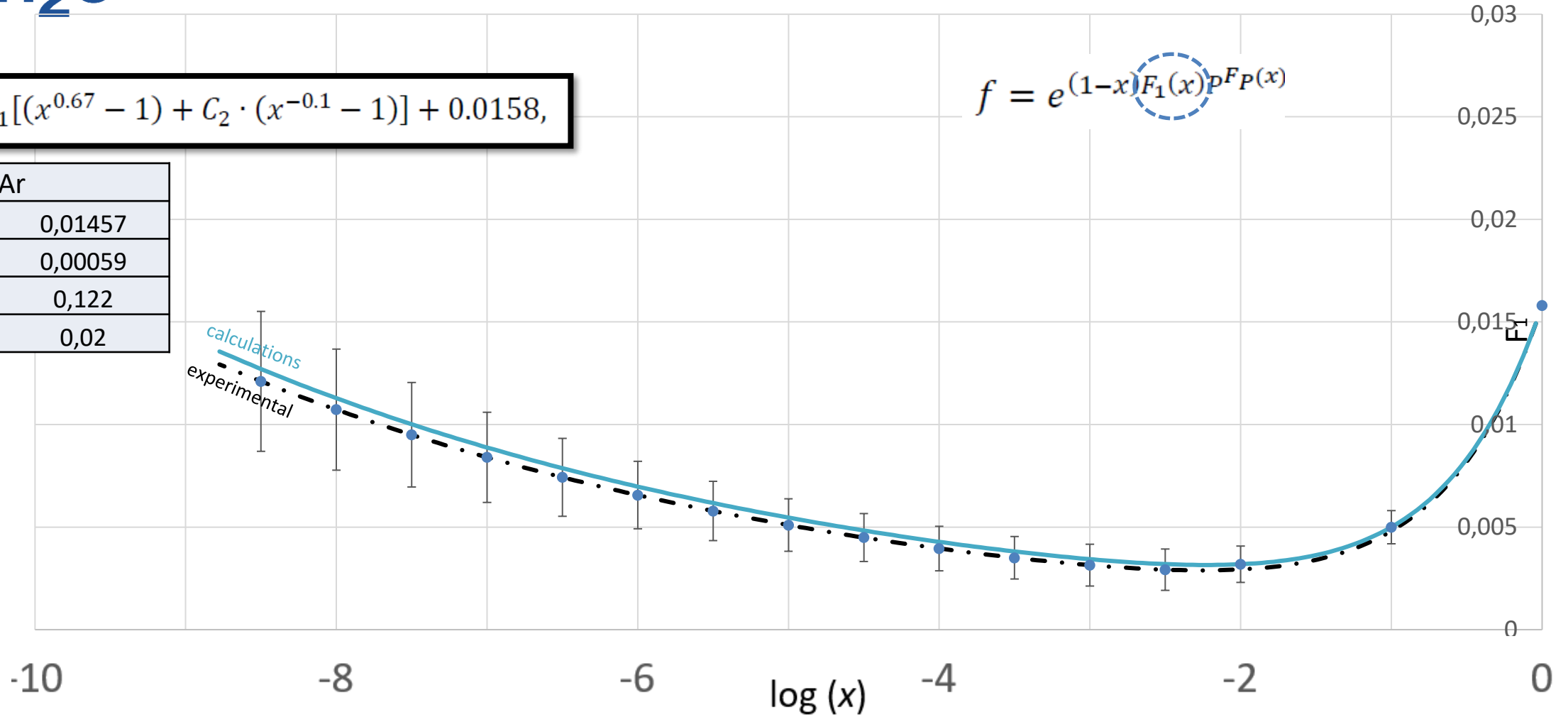
Ar	
C ₁	0,01457
u(c ₁)	0,00059
C ₂	0,122
u(c ₂)	0,02



$$F_1(x) = C_1[(x^{0.67} - 1) + C_2 \cdot (x^{-0.1} - 1)] + 0.0158,$$

$$f = e^{(1-x)F_1(x)P^{FP}(x)}$$

Ar	
C ₁	0,01457
u(c ₁)	0,00059
C ₂	0,122
u(c ₂)	0,02



Gas selection:

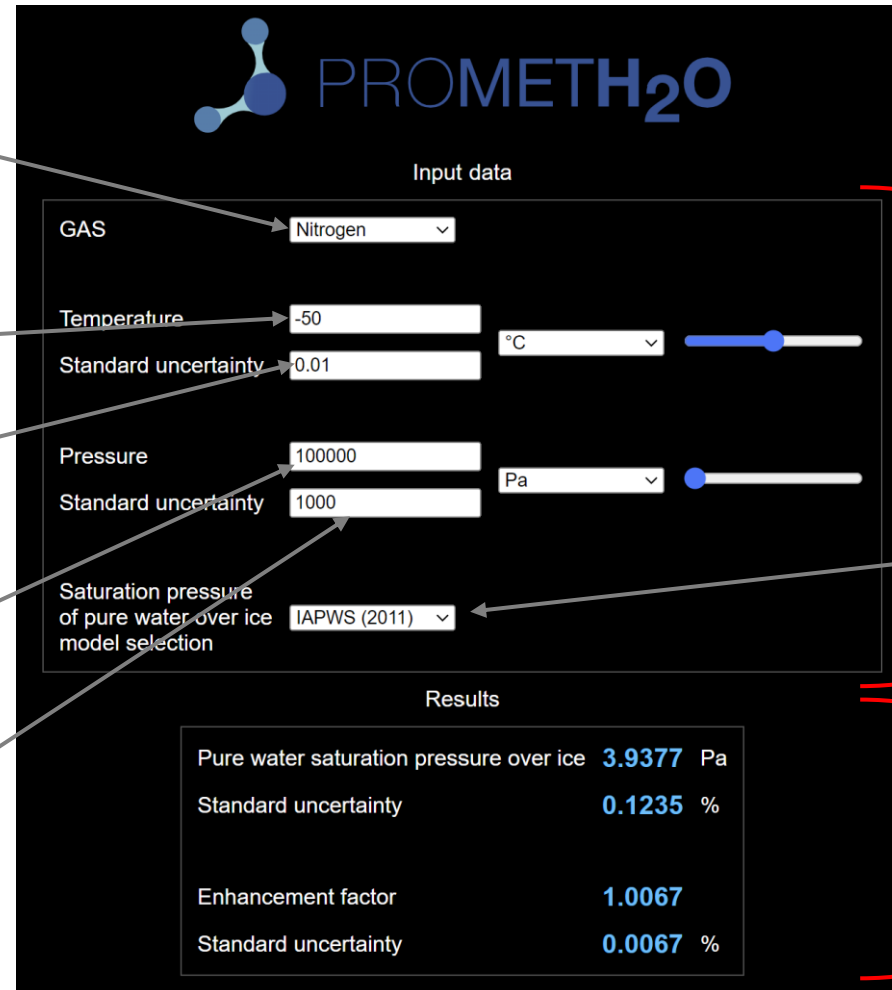
- CO₂-free air
- Nitrogen
- Argon

Input temperature, T
(range: -100÷0 °C)

Temperature standard uncertainty, u_T

Input pressure, P
(range 1÷10 bar)

Pressure standard uncertainty, u_P



The screenshot shows the PROMETH2O web-app interface. The 'Input data' section includes a dropdown for 'GAS' (Nitrogen), a temperature input field (-50) with a unit dropdown (°C) and a slider, a standard uncertainty input field (0.01), a pressure input field (100000) with a unit dropdown (Pa) and a slider, and a standard uncertainty input field (1000). The 'Saturation pressure of pure water over ice model selection' dropdown is set to 'IAPWS (2011)'. The 'Results' section displays the following data:

Pure water saturation pressure over ice	3.9377 Pa
Standard uncertainty	0.1235 %
Enhancement factor	1.0067
Standard uncertainty	0.0067 %

Input data section

Model selection for the calculation of the saturation pressure of pure water over ice, e_i :

- Wexler (ITS90)
- Sonntag (1994)
- IAPWS (2011)
- Huang (2018)

Results section



SCAN ME



- A functional equation has been derived based on the large datasets from the numerical calculations of the equilibrium over a planar pool of liquid/solid water.
- Several measurement setups have been made to perform water vapor enhancement factor measurements for argon, nitrogen, and hydrogen; all of them provide well-documented traceability to the SI system of units.
- While some partners are actively carrying out the experiments, three of them have already delivered excellent results that are in great agreement with each other and with the numerical calculations.
- The relative standard uncertainty, considering the current datasets for the gas-specific equations, is as low as 0.02% to 0.14% at atmospheric pressure elevated to 0.89% at 1 MPa and 1 ppm . This is significantly lower than that of Greenspan's, which is 1% in its entire range.
- Our WebApp is already available at www.prometh2o.unicas.it



PROMETH₂O

What a relief!



VTT

bey⁰nd the obvious

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EMPIR



EURAMET

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