PROMETH2O

20IND06 PROMETH2O

Metrology for trace water in ultra-pure process gases

Final Workshop

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

Overview of our joint effort

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 and UL** Confirmed the measurements of water vapor enhancement down to -80 °C in nitrogen and argon at various pressures using their existing standards. **(2P → *f**)**
6. **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)**
7. **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.
8. **UNICAS** launched the **PROMETH2O WebApp** to facilitate the end-user access to the functional equations

The Big Picture

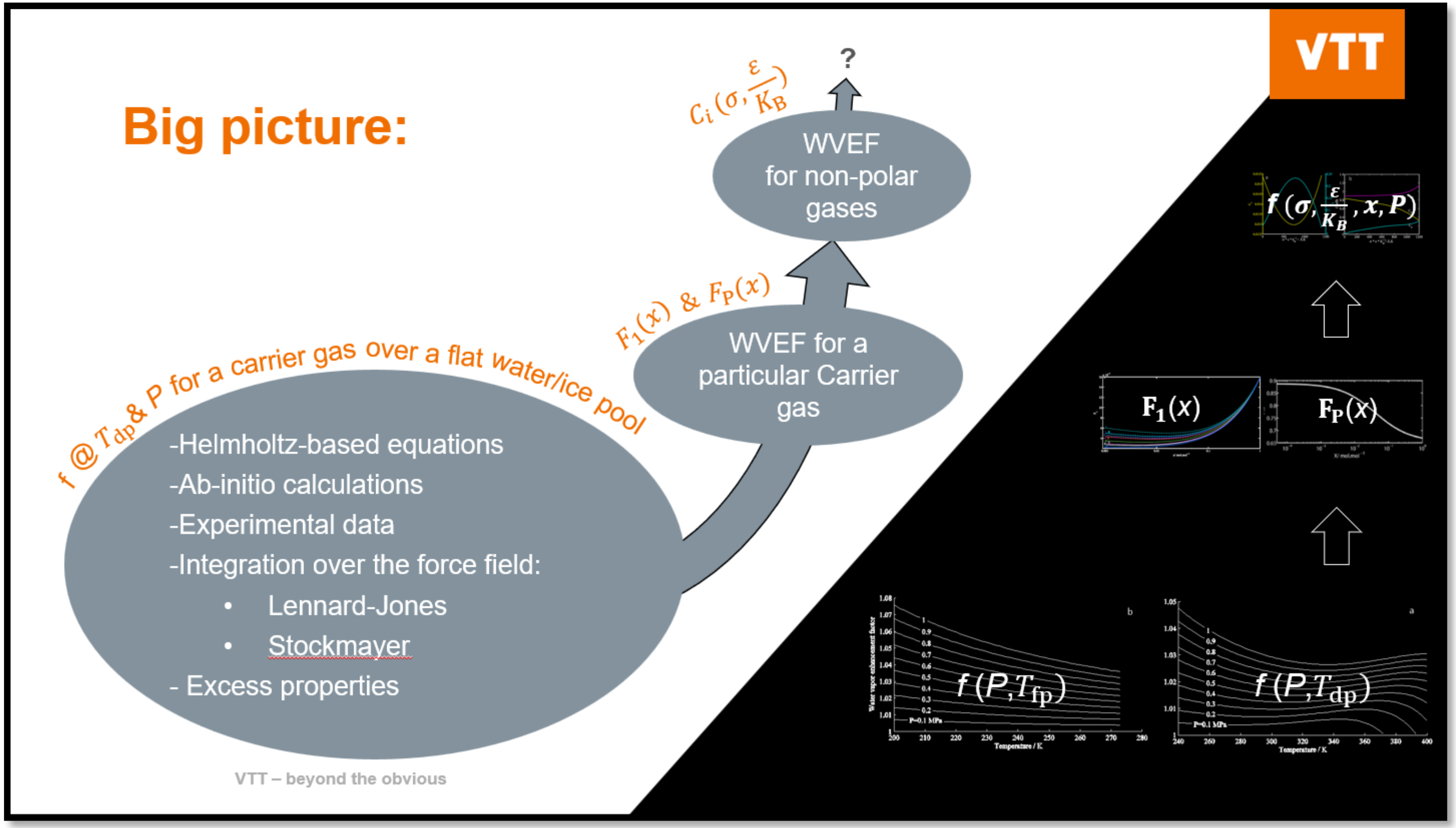
New experimental data for:
Nitrogen: *f.f**
Argon: *f.f**
Hydrogen:*f*

Validation of the calculations

Finetuning the numerical coefficients

Uncertainty estimation of the equtions

Documentation and **WebApp**



f Calculations: Method I

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

$$f_1 = e^{\left[(1+\mathrm{K}_T P_{\mathrm{ws}})(p-P_{\mathrm{ws}})-0.5\mathrm{K}_T\left(P^2-P_{\mathrm{ws}}^2\right)\right]\frac{\bar{\nu}_{\mathrm{c}}}{RT}}, \quad \text{Eq.1.1}$$

$$f_2 = 1 - \frac{x_{\mathrm{a}} \cdot P}{K_{\mathrm{a}}}, \quad \text{Eq.1.2}$$

$$f_3 = e^{\frac{x_{\mathrm{a}}^2 P}{RT} B_{\mathrm{aa}}}, \quad \text{Eq.1.3}$$

$$f_4 = e^{-2\frac{x_{\mathrm{a}}^2 P}{RT} B_{\mathrm{aw}}}, \quad \text{Eq.1.4}$$

$$f_5 = e^{-\frac{P-P_{\mathrm{ws}}-x_{\mathrm{a}}^2 P}{RT} B_{\mathrm{ww}}}, \quad \text{Eq.1.5}$$

$$f_6 = e^{\frac{x_{\mathrm{a}}^3 P^2}{(RT)^2} C_{\mathrm{aaa}}}, \quad \text{Eq.1.6}$$

$$f_7 = e^{3\frac{x_{\mathrm{a}}^2 (1-2X_{\mathrm{a}}) P^2}{2(RT)^2} C_{\mathrm{aaw}}}, \quad \text{Eq.1.7}$$

$$f_8 = e^{-3\frac{x_{\mathrm{a}}^2 (1-x_{\mathrm{a}}) P^2}{(RT)^2} C_{\mathrm{aww}}}, \quad \text{Eq.1.8}$$

$$f_9 = e^{-\frac{(1+2x_{\mathrm{a}})(1-x_{\mathrm{a}})^2 P^2 - P_{\mathrm{ws}}{}^2}{2(RT)^2} C_{\mathrm{www}}}, \quad \text{Eq.1.9}$$

$$f_{10} = e^{-\frac{x_{\mathrm{a}}^2 (1-3x_{\mathrm{a}})(1-x_{\mathrm{a}}) P^2}{(RT)^2} B_{\mathrm{aa}} B_{\mathrm{ww}}}, \quad \text{Eq.1.10}$$

$$f_{11} = e^{-2x_{\mathrm{a}}^3 \frac{(2-3X_{\mathrm{a}}) P^2}{(RT)^2} \cdot B_{\mathrm{aa}} \cdot B_{\mathrm{aw}}}, \quad \text{Eq.1.11}$$

$$f_{12} = e^{6x_{\mathrm{a}}^2 \frac{(1-x_{\mathrm{a}})^2 P^2}{(RT)^2} B_{\mathrm{aw}} B_{\mathrm{ww}}}, \quad \text{Eq.1.12}$$

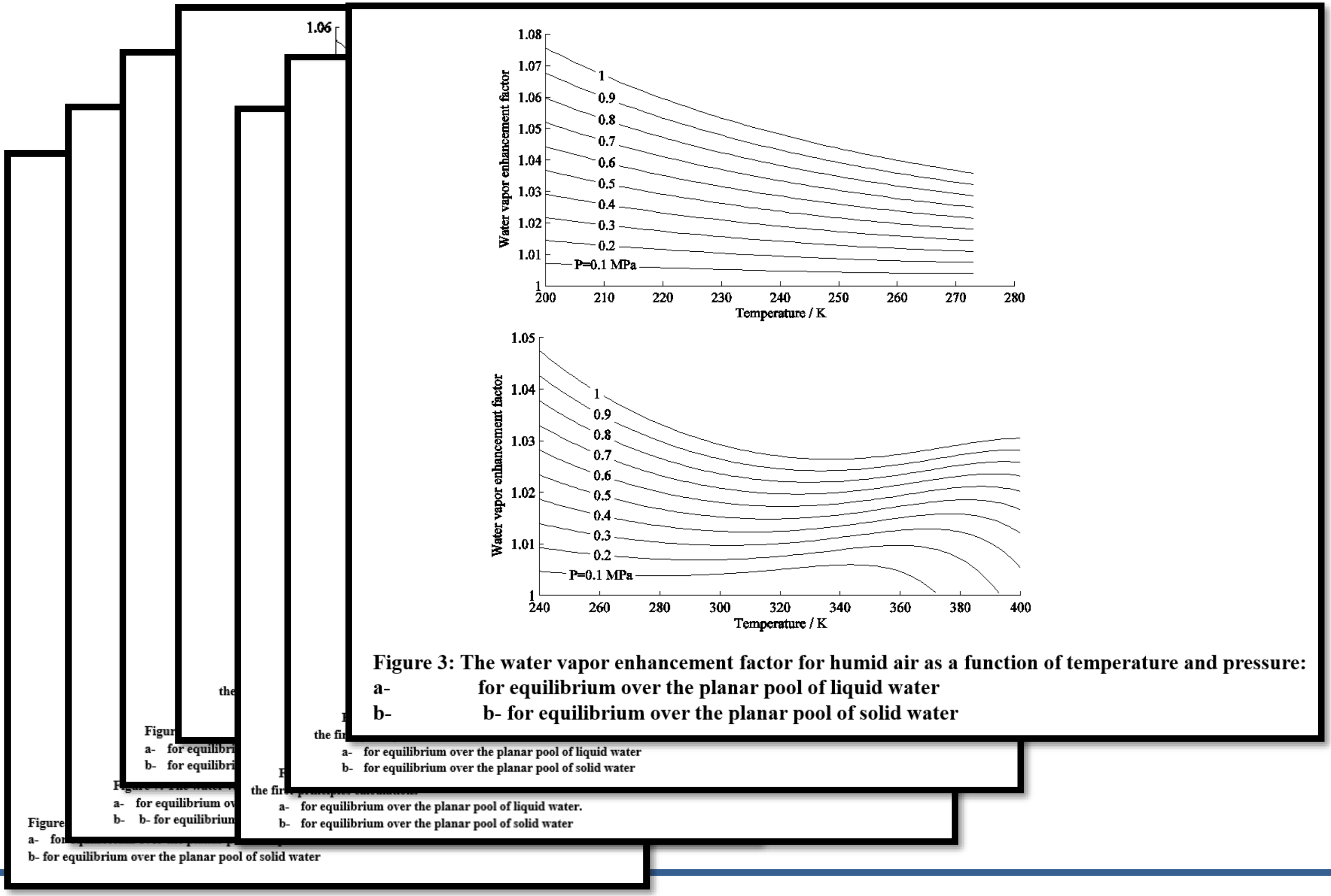
$$f_{13} = e^{-\frac{3x_{\mathrm{a}}^4 P^2}{2(RT)^2} B_{\mathrm{aa}}^2}, \quad \text{Eq.1.13}$$

$$f_{14} = e^{-2x_{\mathrm{a}}^2 \frac{(1-x_{\mathrm{a}})(1-3x_{\mathrm{a}}) P^2}{(RT)^2} B_{\mathrm{aw}}{}^2}, \quad \text{Eq.1.14}$$

$$f_{15} = e^{-\frac{P_{\mathrm{ws}}{}^2 - (1+3x_{\mathrm{a}})(1-x_{\mathrm{a}})^3 P^2}{2(RT)^2} B_{\mathrm{ww}}{}^2}, \quad \text{Eq.1.15}$$

f Calculations: Method I results

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



f Calculations: Method II

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

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

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

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

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

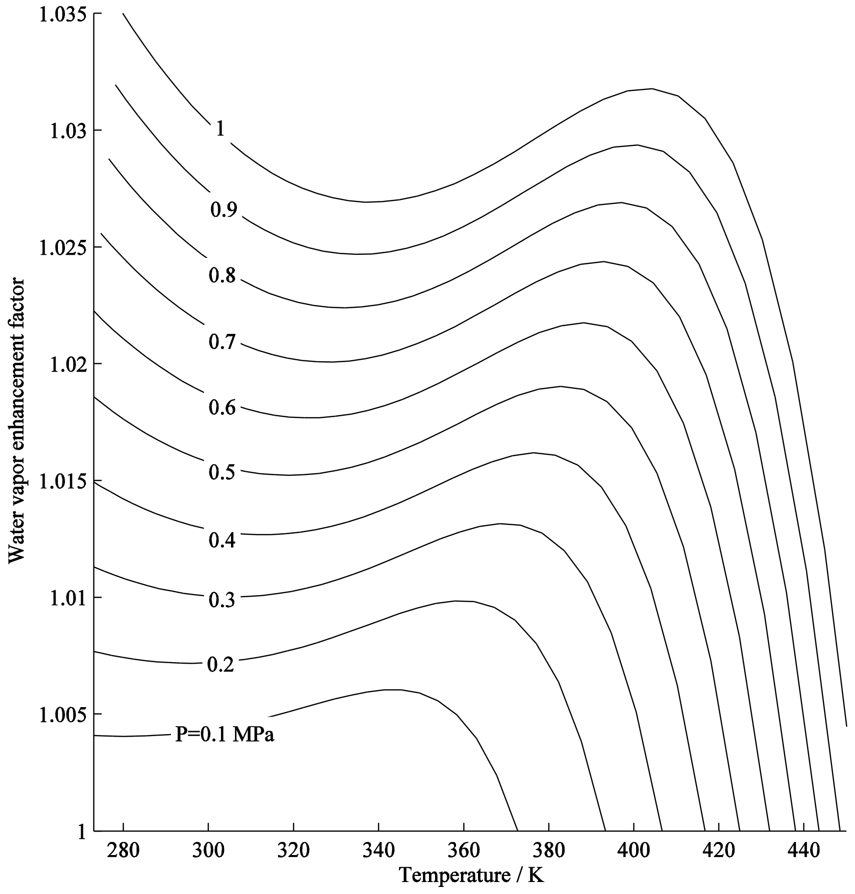


Figure 4: The water vapor enhancement factor for equilibrium over a planar pool of liquid water based on the second method

The Functional Equation:

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

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

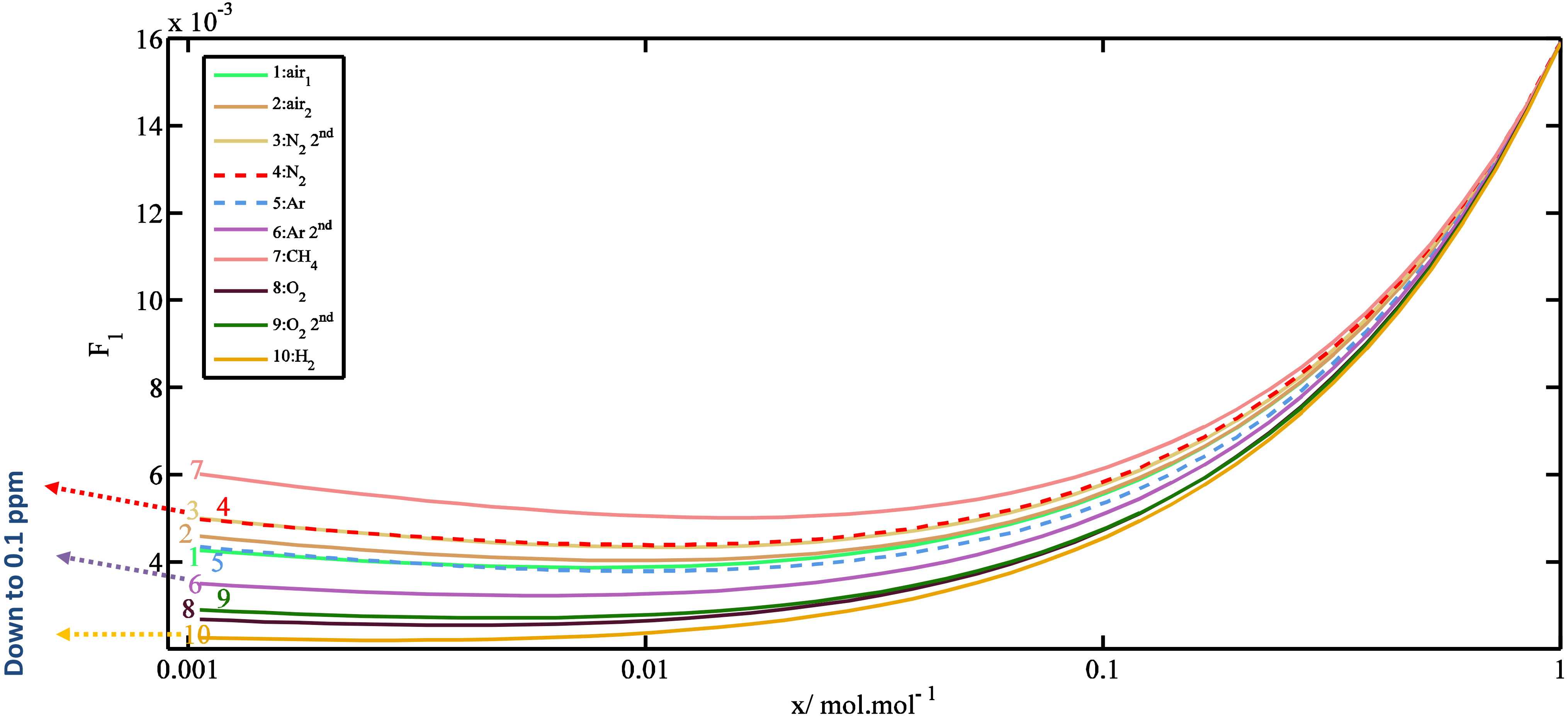
$$F_P(x) = F_{P,d} + \bar{a}\left[\tanh\left(\bar{b} \cdot \ln(x) + \bar{c}\right) + 1\right] \approx F_{P,d} + \frac{-0.1963 \cdot x^{c_3}}{c_3 \cdot (x^{c_3} + c_4)}. \quad \text{Eq.18}$$

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

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

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

The atmospheric factor (F_1):



The pressure factor (F_P) :

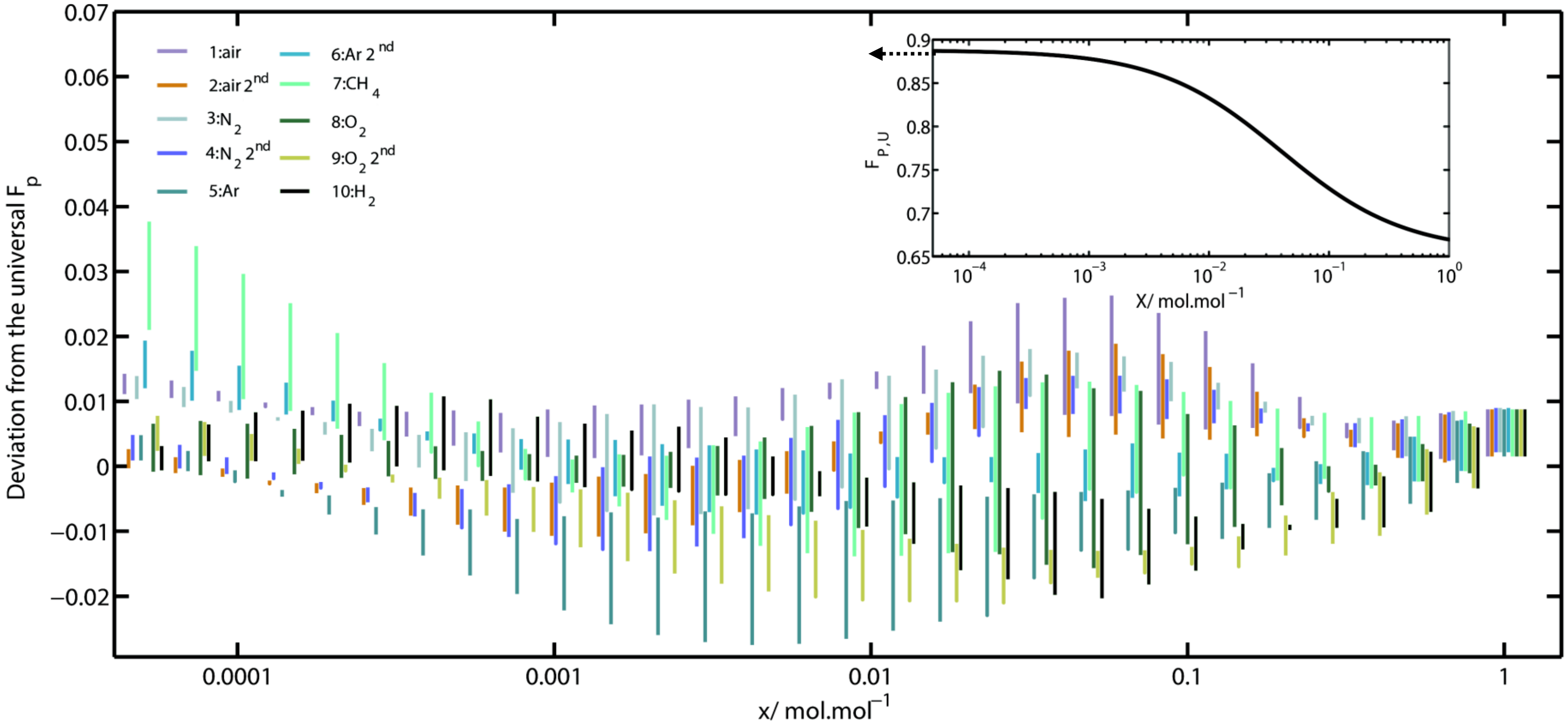
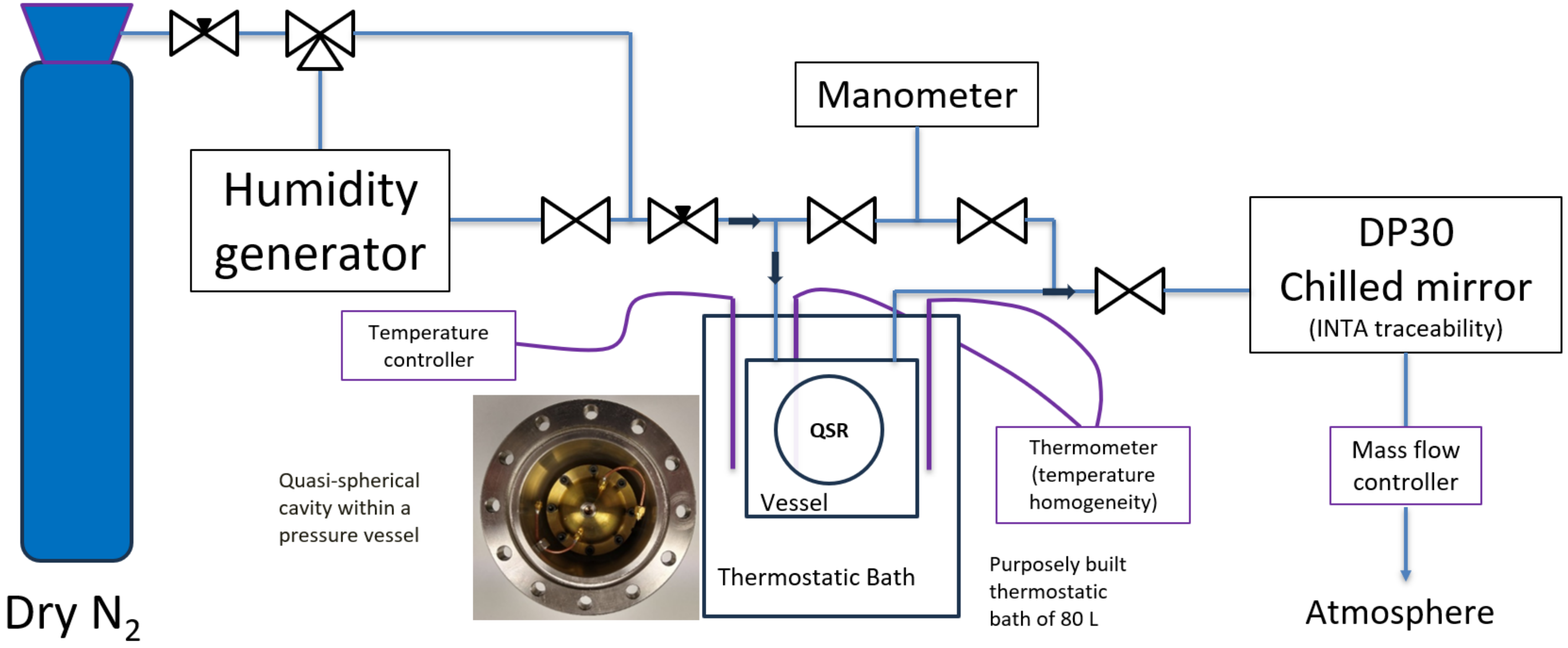


Figure 16: The pressure factor. F_P. for various carrier gasses. bars are indicative of the pressure dependence; uncertainty levels are way bigger. Bars are moved horizontally for the sake of visualization.

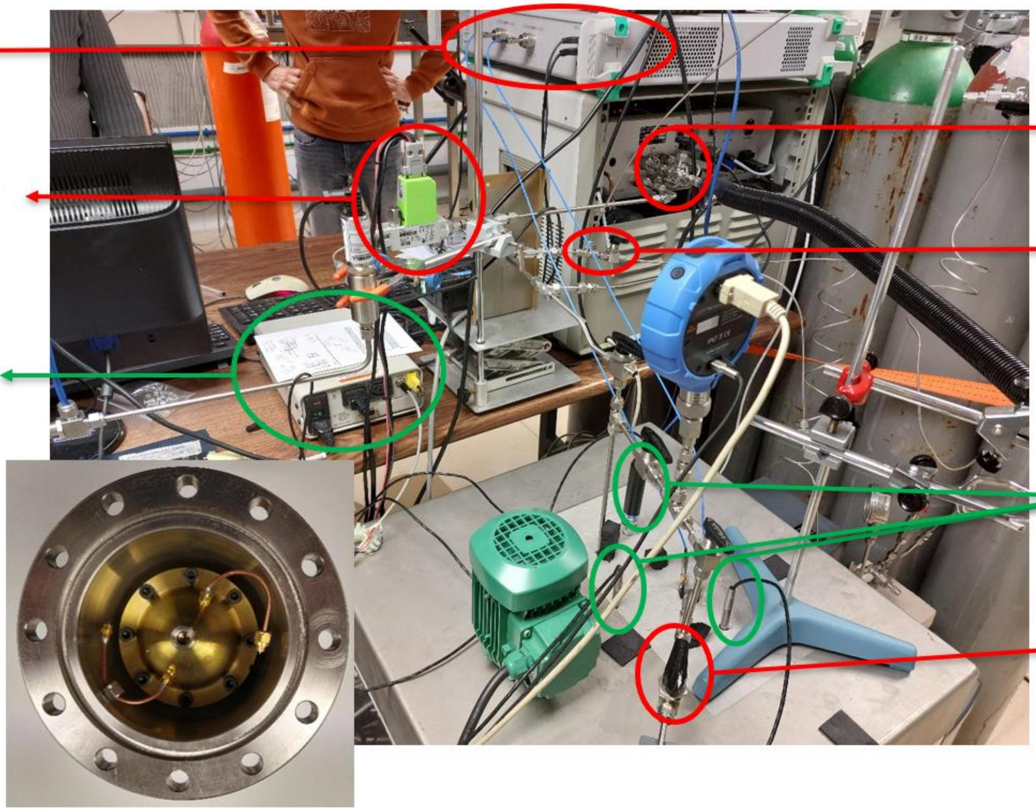
Experimental Setup: UVa and INTA

BioEcoUVa | Universidad de Valladolid | TermoCal

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



Experimental Setup: UVa and INTA

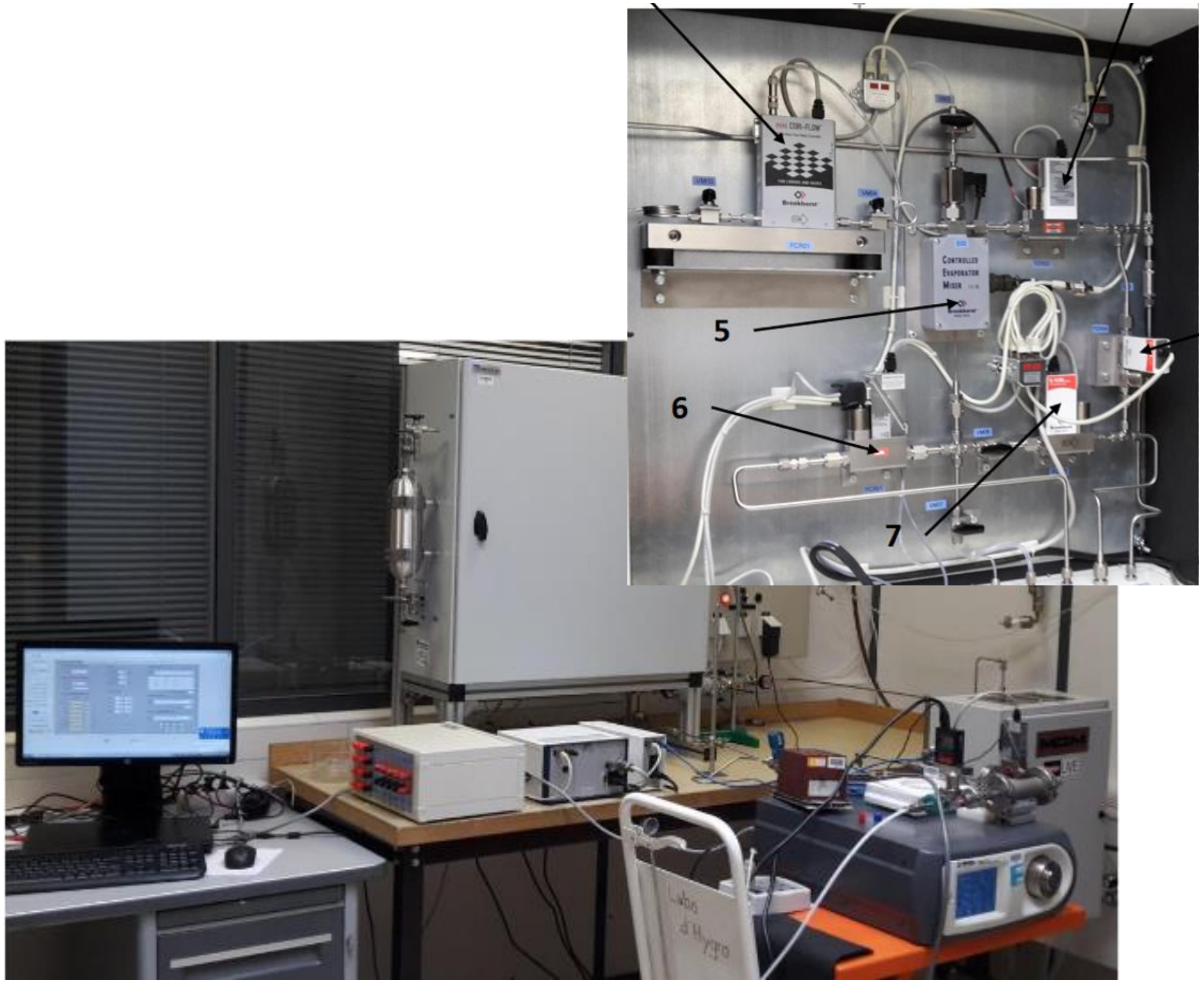


The measurement setup consists of the quasi-spherical cavity within a pressure vessel immersed in a purposely built thermostatic bath of 80 L. Inside the bath. there are three temperature probes. one used to control and maintain the temperature at the desired setpoint. and the other two to check for 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.

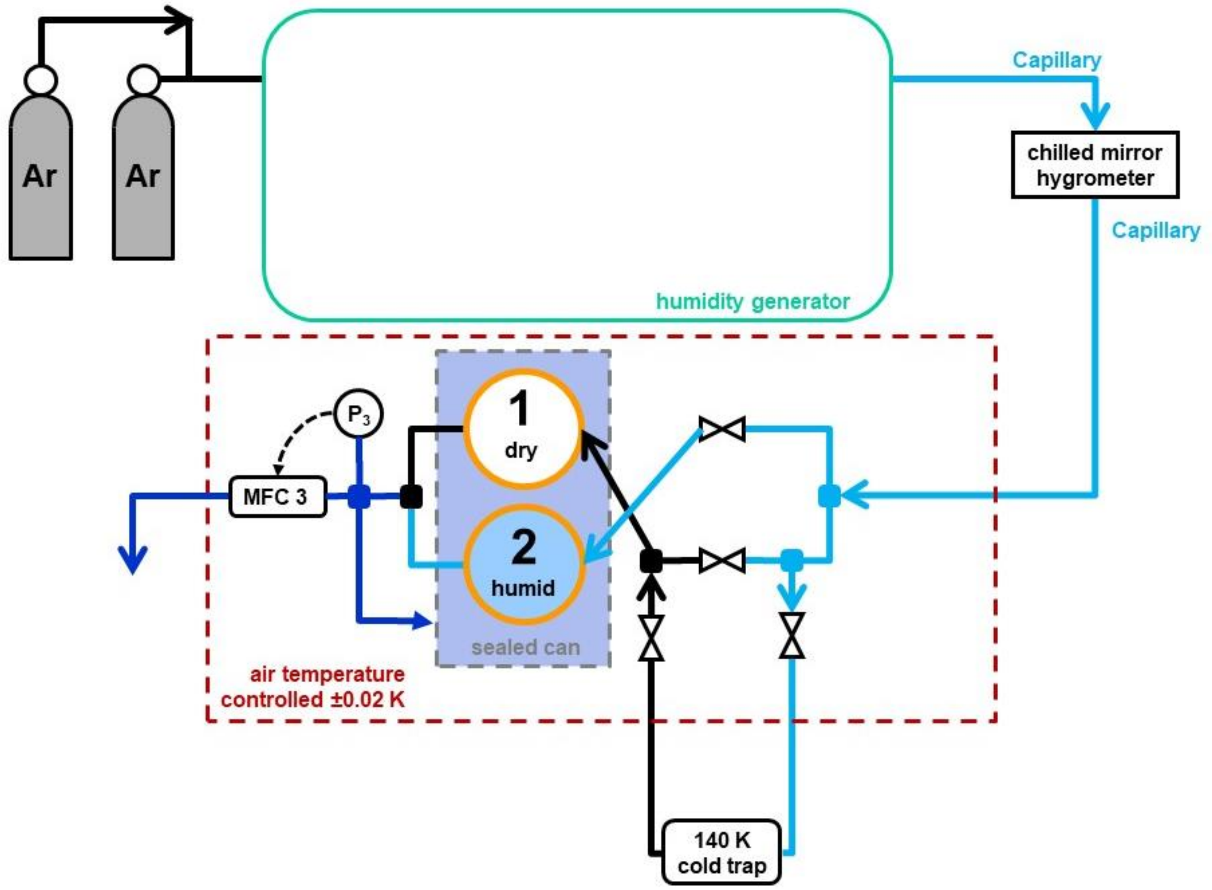
Experimental Setup: CNAM and CETIAT

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



Experimental Setup: CNAM and CETIAT



-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 N_2 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.

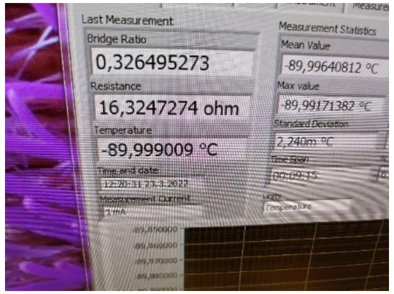
-the temperature of the spheres is measured using four pt100 temperature sensors in series on each sphere. Resonance frequencies and measured with lock-in amplifiers. The sealed can is connected to the outlet pressure.

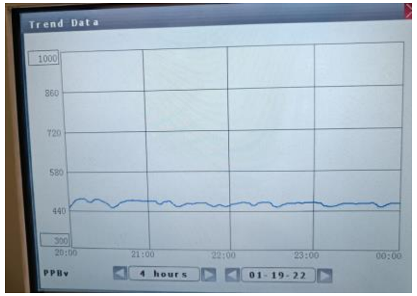
Experimental Setup: CMI

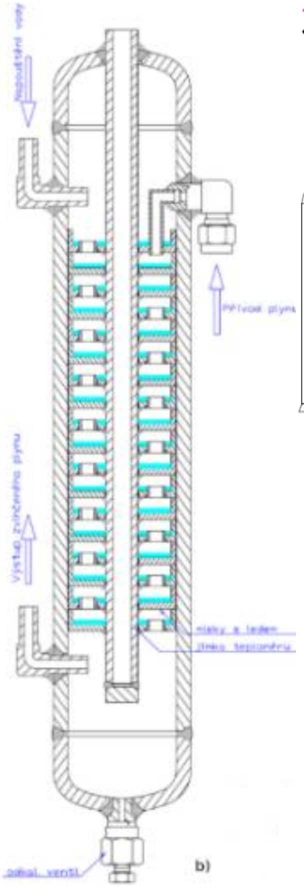
Primary humidity generator. 1P1T type. saturation-based principle:

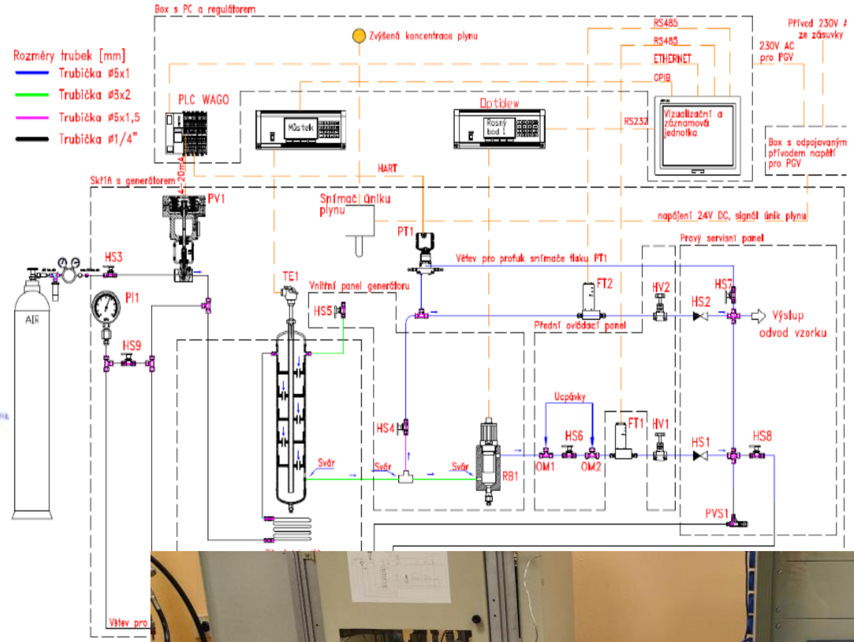
- Pressure: 15 MPa max.
- Humidity range: (-80 to 30) °C dp/fp
- Gas matrix: Air. N_2. Ar. CH_4. natural gas
- Pressure 0.05 %
- Temperature
  - SPRT
  - MBW
- Mixing ratio Halo 3 H_2O

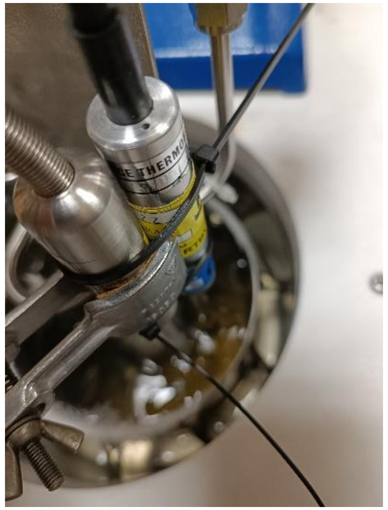
Temperature range. °C	Pressure range. Kpa	Media
-60 to -90	200 to 800	Nitrogen
-60 to -90	200 to 800	Argon

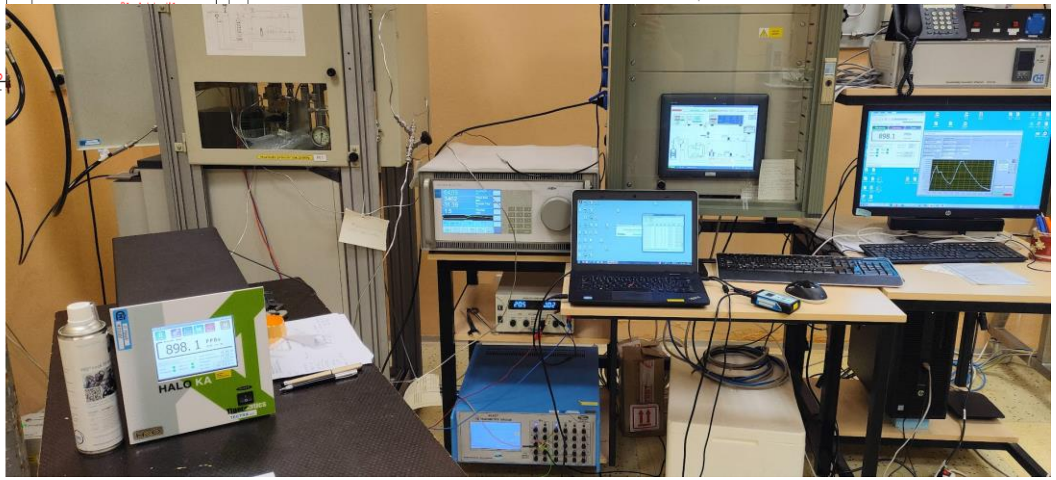






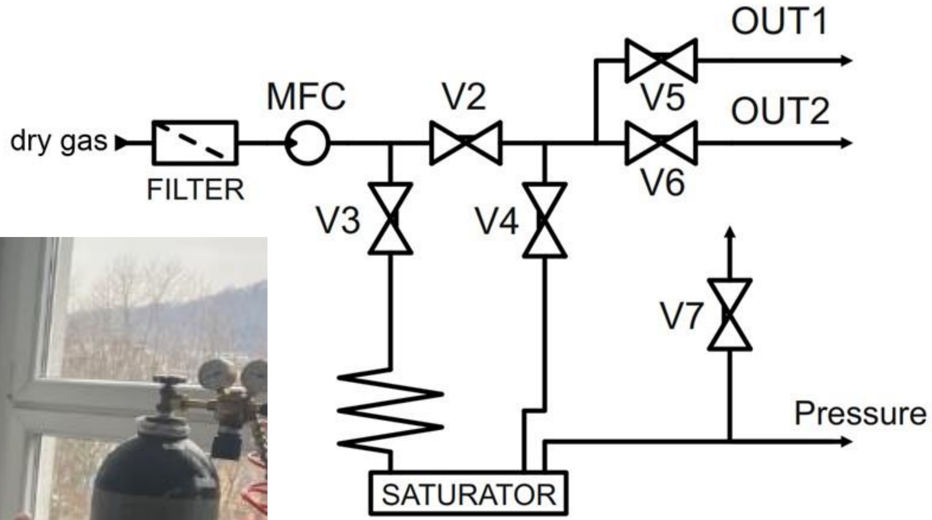


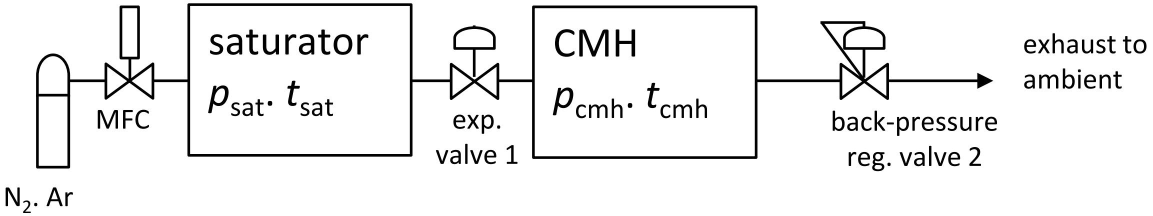




Experimental Setup: UL

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



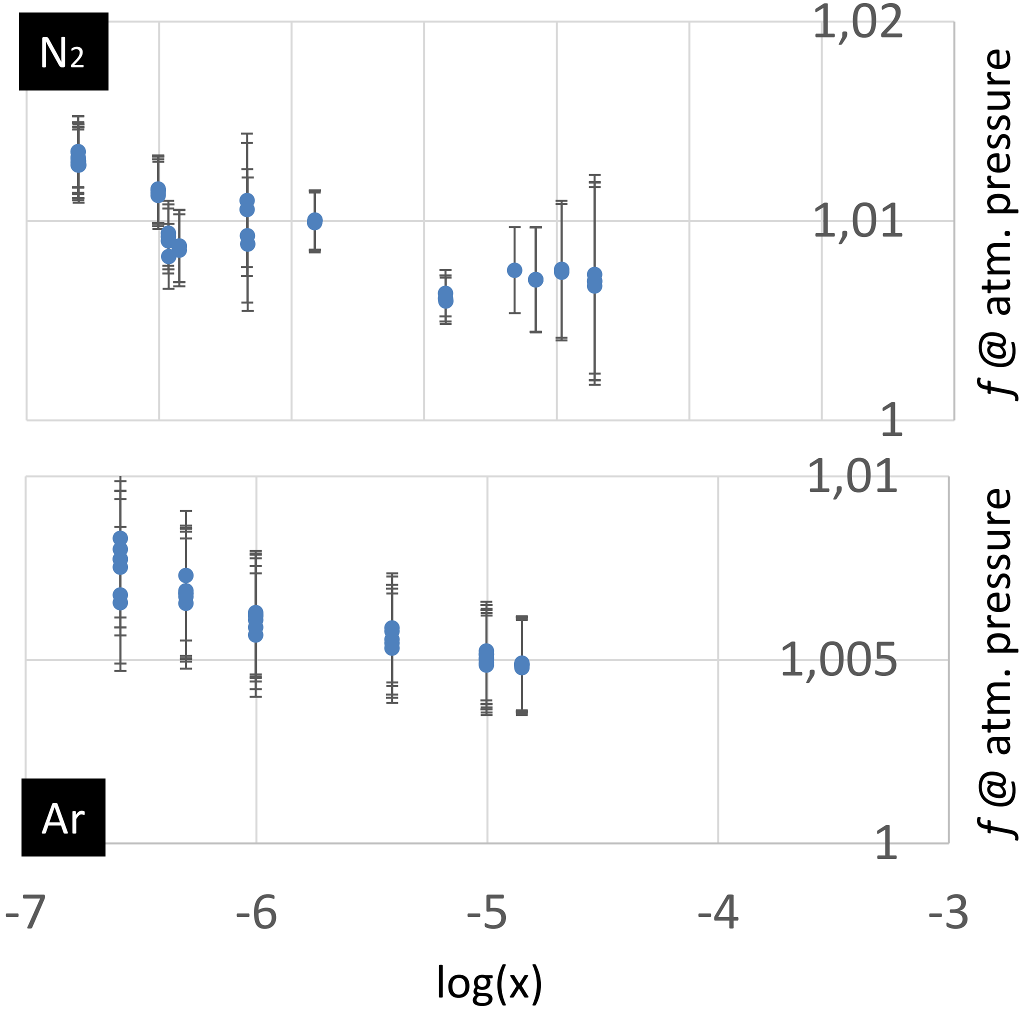


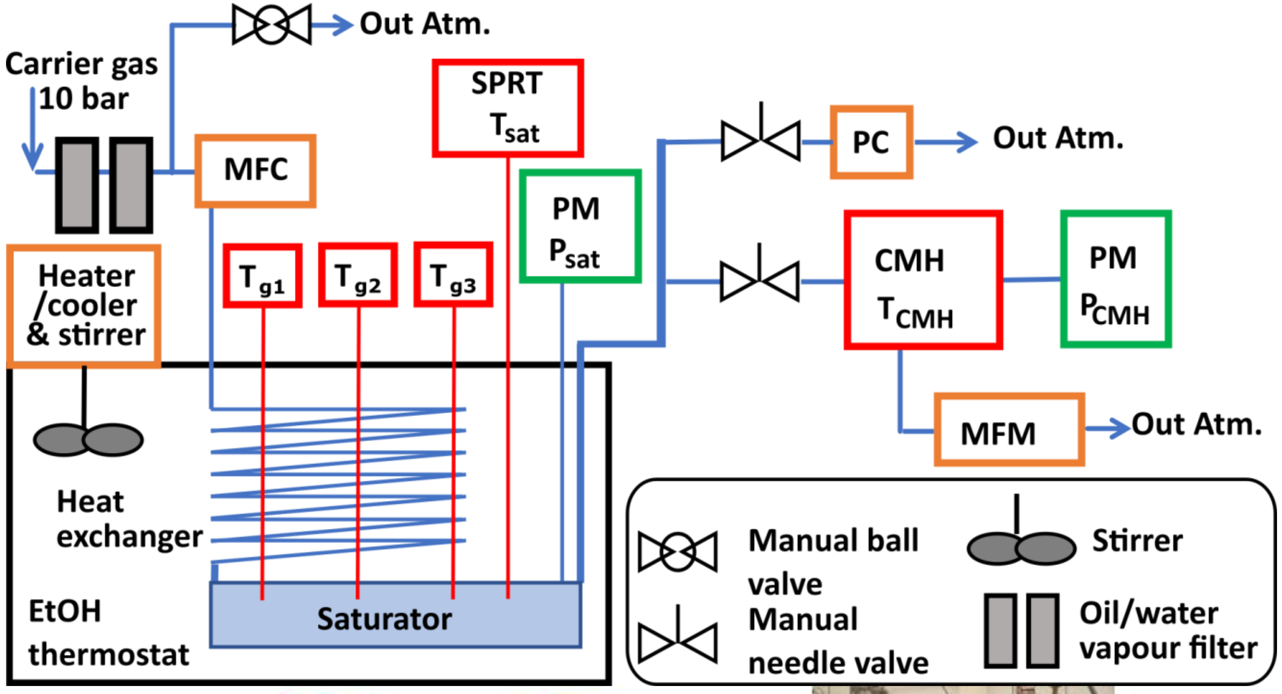
Preliminary results @ -30 °C. 10 bar:

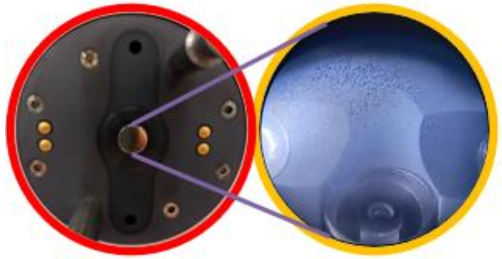
f* **= 1.0435**	**vs.**	**1.0451**	**(N2 ab-initio)**
		1.045	**(N2 PROMETH2O)**
		1.0396	**(Greenspan)**

UNIVERSITY OF LJUBLJANA | FE Faculty of Electrical Engineering

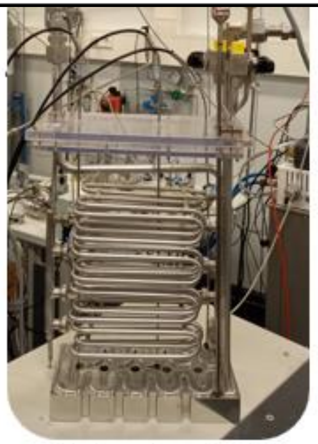
Experimental Setup: VSL







Chilled Mirror Hygrometer (CMH)
MBW 373 LX



Saturator (sat)

Uncertainty budget for f^* measured at VSL

$$f^*_{\text{measured}} = \frac{e\left(T^{\text{CMH}}_{d.\,\text{measured}}\right)_{\text{formula}}}{e\left(T^{\text{sat}}_{d.\,\text{measured}}\right)_{\text{formula}}} \cdot \frac{P^{\text{sat}}_{\text{measured}}}{P^{\text{CMH}}_{\text{measured}}} = \frac{e\left(T_d^{\text{CMH}} + \delta T_d^{\text{CMH}}\right) + \delta e\left(T_d^{\text{CMH}}\right)}{e\left(T_d^{\text{sat}} + \delta T_d^{\text{sat}}\right) + \delta e\left(T_d^{\text{sat}}\right)} \cdot \frac{P^{\text{sat}} + \delta P^{\text{sat}}}{P^{\text{CMH}} + \delta P^{\text{CMH}}}$$

T_d^{sat}
$\delta T^s_{\text{sat. cal}}$
$\delta T^s_{\text{sat. drift}}$
$\delta T^s_{\text{sat. self-heat}}$
$\delta R^s_{\text{s.cal}}$
$\delta W^s_{\text{bridge. Cal}}$
$\delta W^{rm}_{\text{bridge. resolution}}$
$\delta T^{rm}_{\text{sat. stability}}$
$\delta T^{rm}_{\text{gradient}}$
δT_d^{sat}

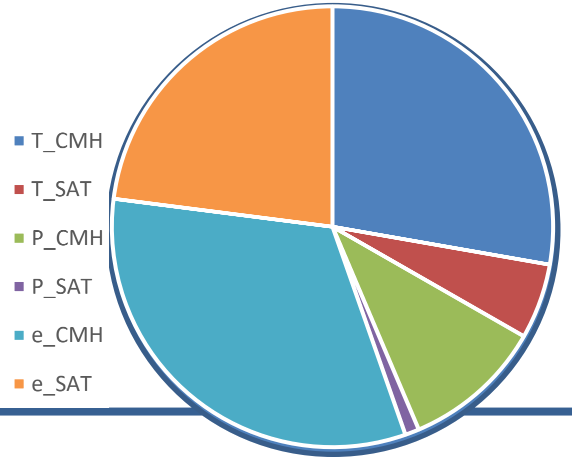
T_d^{CMH}
$\delta T^s_{\text{efficiency}}$
$\delta T^{rm}_{\text{contamination}}$
$\delta T^{rm}_{\text{CMH. stability}}$
$\delta T^{rm}_{\text{CMH. resolution}}$
$\delta T^{rm}_{\text{CMH. flow}}$
δT_{fit}
$\delta \Delta P^s_{\text{CMH}}$
$\delta \Delta P^s_{\text{sat}}$
δT_d^{CMH}

$e(T_d^{\text{sat}})$
$\delta T^{\text{sat}}_{\text{formula}}$

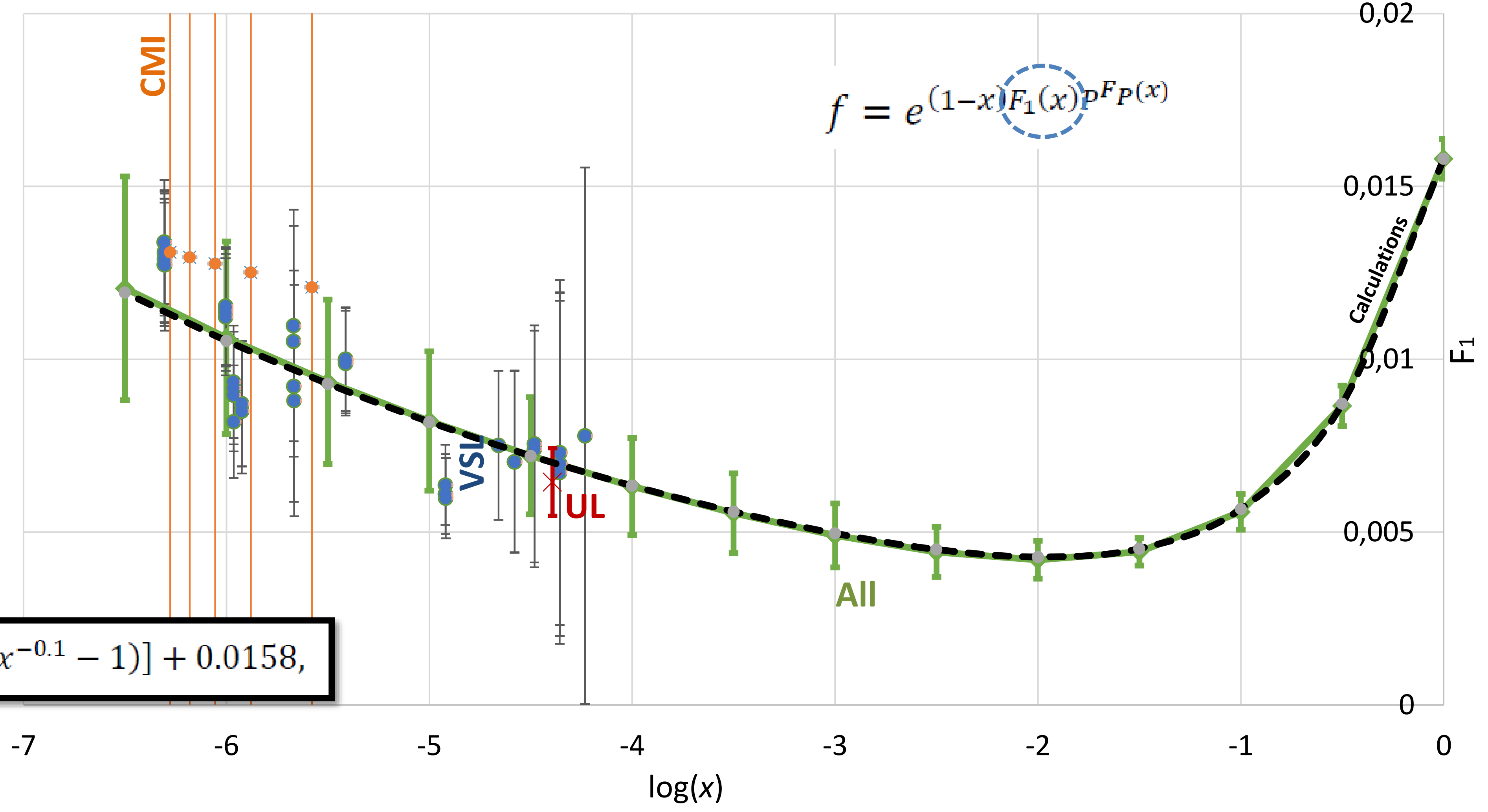
$e(T_d^{\text{CMH}})$
$\delta T^{\text{CMH}}_{\text{formula}}$

$P^{\text{sat}}_{\text{measured}}$
δP^s_{sat}

$P^{\text{CMH}}_{\text{measured}}$
δP^s_{CMH}



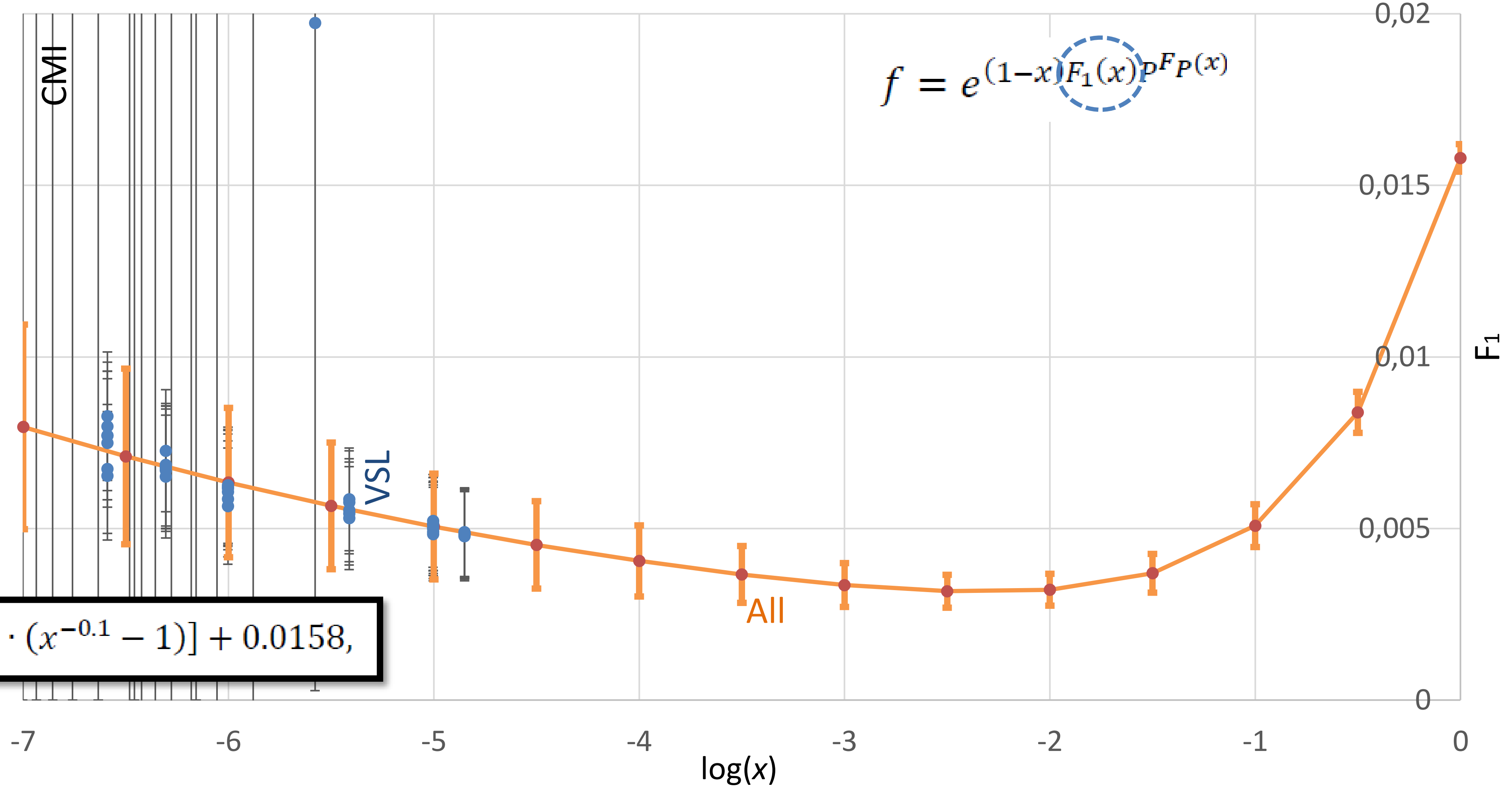
N2: Results



N2	
C1	0.01396
u(c1)	2.5E-04
C2	0.2105
u(c2)	0.026

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

Ar: Results

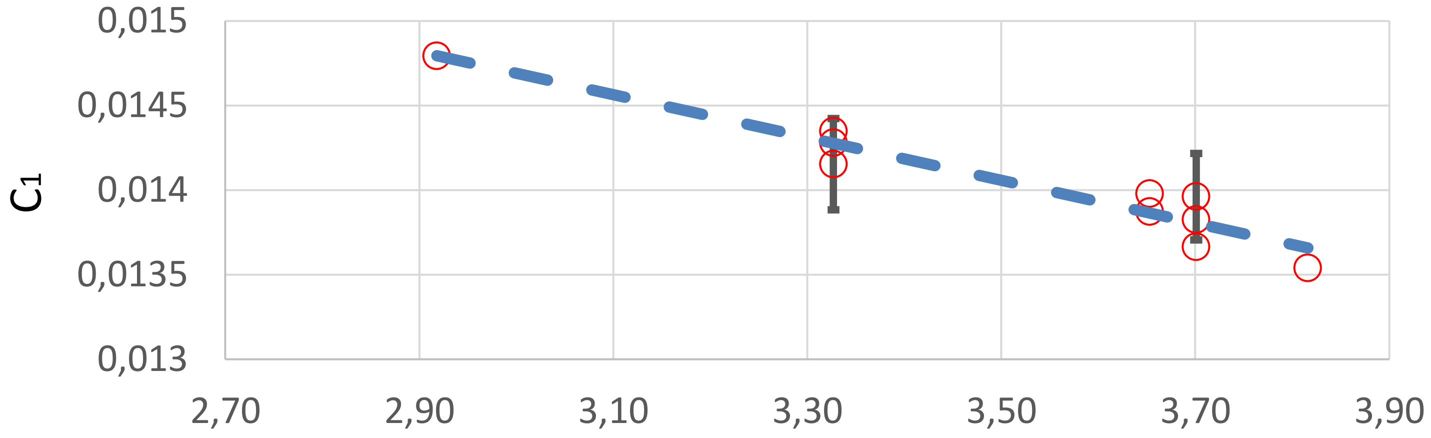


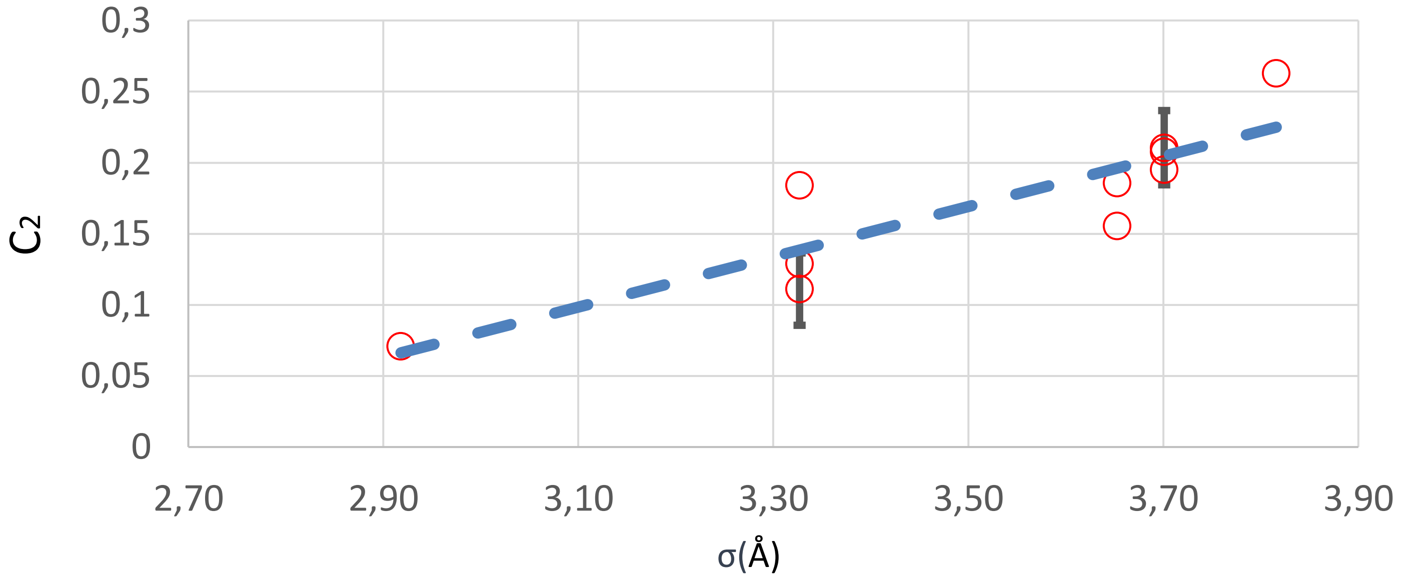
Ar	
C_1	0.01415
$u(c_1)$	2.70E-04
C_2	0.1111
$u(c_2)$	0.0254

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

Towards a Master Equation: WVEF for Non-Polar Gases

	C_1	C_2	
Air	0.013873	0.155554	Experimental
Air	0.013978	0.185792	Ab-initio calculations
Nitrogen	0.013665	0.195243	LJ potential
Nitrogen	0.013826	0.207725	Ab-initio calculations
Nitrogen	0.013961	0.210513	PROMETH2O
Argon	0.01428	0.184174	LJ potential
Argon	0.014347	0.129017	Ab-initio calculations
Argon	0.014153	0.1111	PROMETH2O
methane	0.013539	0.26287	LJ potential
hydrogen	0.014792	0.070917	LJ potential





Web-app available at www.prometh2o.unicas.it

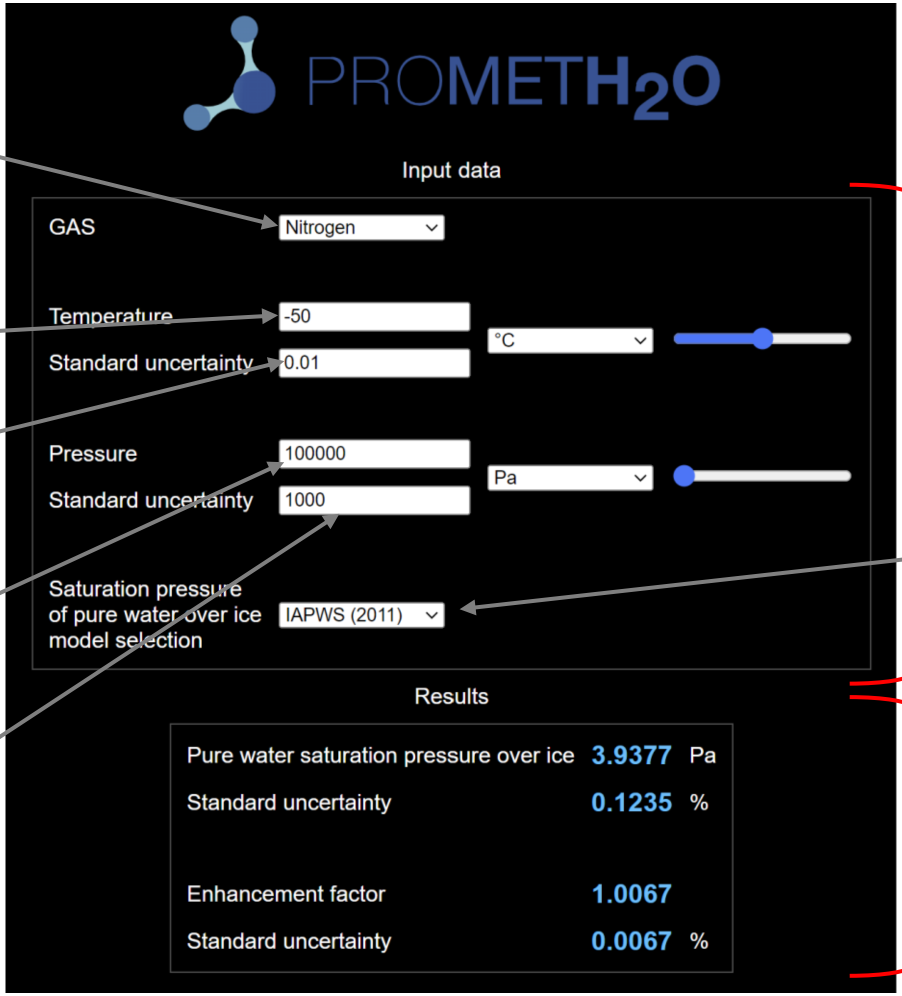
Gas selection:
- CO2-free air
- Nitrogen
- Argon

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

Temperature standard uncertainty, u_T

Input pressure, P
(range 1÷10 bar)

Pressure standard uncertainty, u_P



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

Fausto Arpino, *f.arpino@unicas.it*

Conclusions:

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

Thank you for your attention

SCAN ME

beyond
the obvious

Shahin Tabandeh
Shahin.tabandeh@vtt.fi
+358 50 313 3634

@VTTFinland

www.vtt.fi

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