PROMETH2O

20IND06 PROMETH2O

WP2

Provision of robust traceability to trace water measurements in real humid gas mixtures

Project Progress Meeting at M18

In person, hosted by VSL

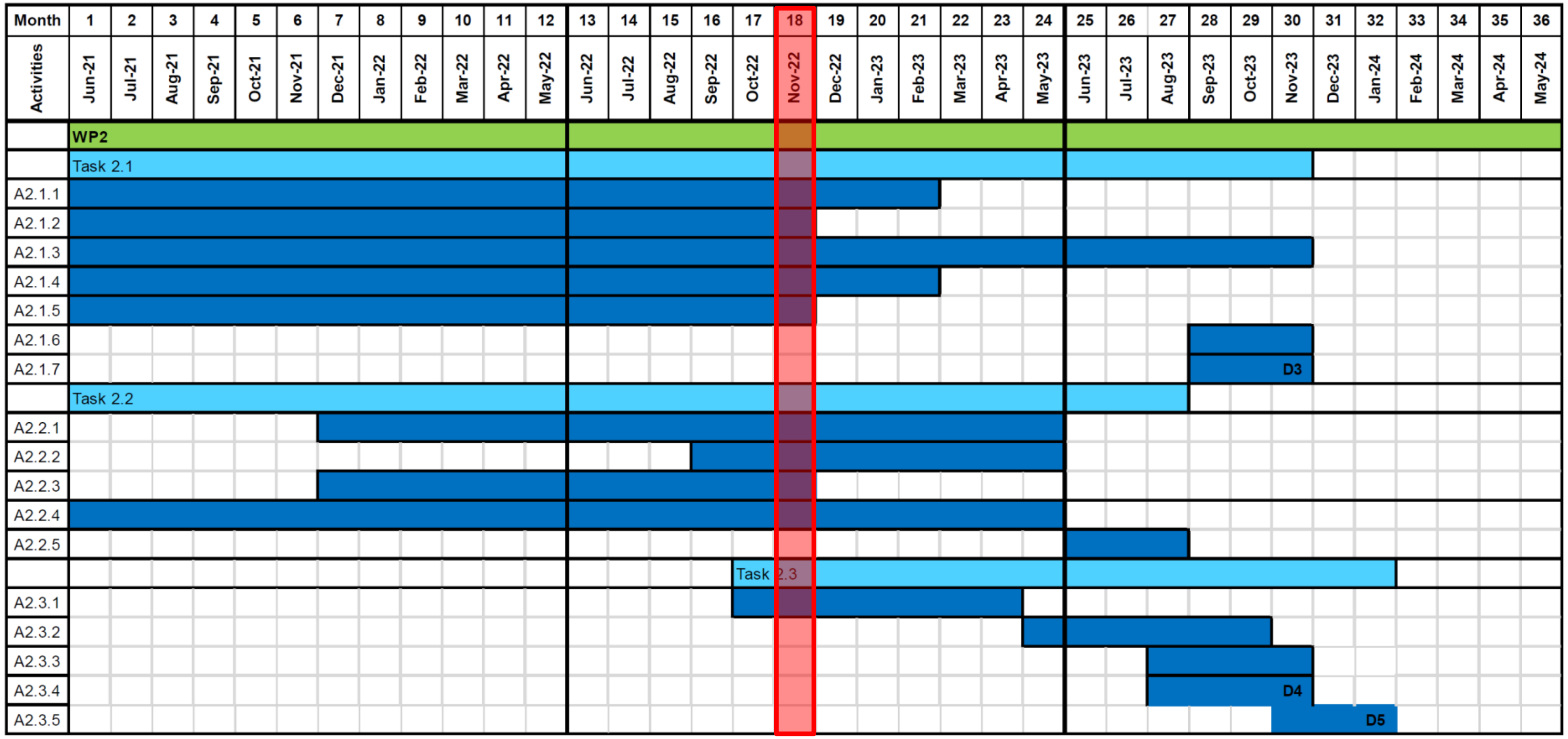
2-3 November 2022

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

The Work Package

Development and validation of primary standards for trace water vapour measurements in ultra-pure gases:

- by using a variety of **complementary generation techniques** (**Task 2.1**)
- by improving the knowledge of the **non-ideal behaviour of humid gas mixtures** (**Task 2.2 - Task 2.3**)



3 Tasks
All active at M18

Activities **2.1.2, 2.1.5** and **2.2.3** accomplished by the end of November 2022.

Task 2.1
Development of primary humidity standards for trace water vapour in an increased range of gas matrices

Task 2.1: Activities

06/21 M1 | 05/22 M12 | 11/22 M18 | 02/23 M21 | 05/23 M24 | 11/23 M30

Task 2.1 Development of primary humidity standards

A2.1.1 Thermodynamic saturation-based generator (T_{fp} = -105 °C, P = 0.5 MPa)

A2.1.2 Thermodynamic saturation-based generator (T_{fp} = -90 °C, P = 1 MPa)

A2.1.3 Coulometric-based generator (x_w = 5 ppb, P =0.11 MPa)

A2.1.4 Permeation-based generator (x_w = 50 ppb)

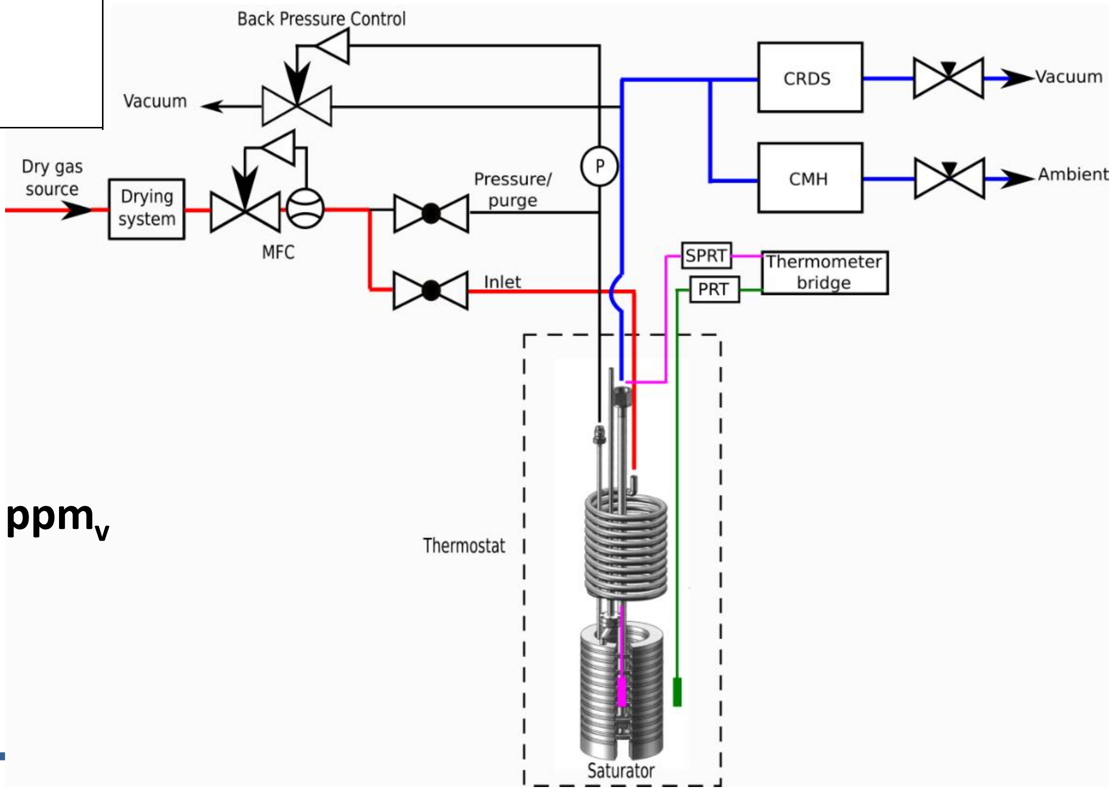
A2.1.5 Mixed flow generator (T_{fp} = -95 °C, P = 1 MPa)

A2.1.6 Report

A2.1.7 **Report sub. to EURAMET D3**

Activity number	Activity description	Partners (Lead in bold)
A2.1.1 M21	INRIM will improve its thermodynamic saturation-based primary standard generator to generate the humid gas mixtures standard in nitrogen and argon at pressures up to 0.5 MPa and to extend the lower limit of frost-point temperature to -105 °C with a standard uncertainty of 0.35 °C. VTT will extend its saturation-based primary standard generator to -100 °C at 0.11 MPa to generate humid gas mixtures in nitrogen and air. INRIM and VTT will use such primary humidity standards to provide traceability to trace water analysers, such as the CC-FS-CRDS spectrometer (A1.1.1), high-quality CMH, and CE-FM spectroscopy hygrometer (A1.1.4) and underpin their validation in A1.2.1 to A1.2.3.	**INRIM**, VTT

Reference: R Cuccaro et al 2018 Meas. Sci. Technol. 29 054002
https://doi.org/10.1088/1361-6501/aaa785



STARTING POINT

LFP HUMIDITY GENERATOR – Mark 1

- Single-pressure, single-pass humidity generator
- **Frost-point temperature between -99 °C and -20 °C**
- **Water vapour mole fraction between 15 ppb_v and 945 ppm_v @1100 hPa**
- Pressure: 200 hPa to 2400 hPa
- Carrier gas: Nitrogen

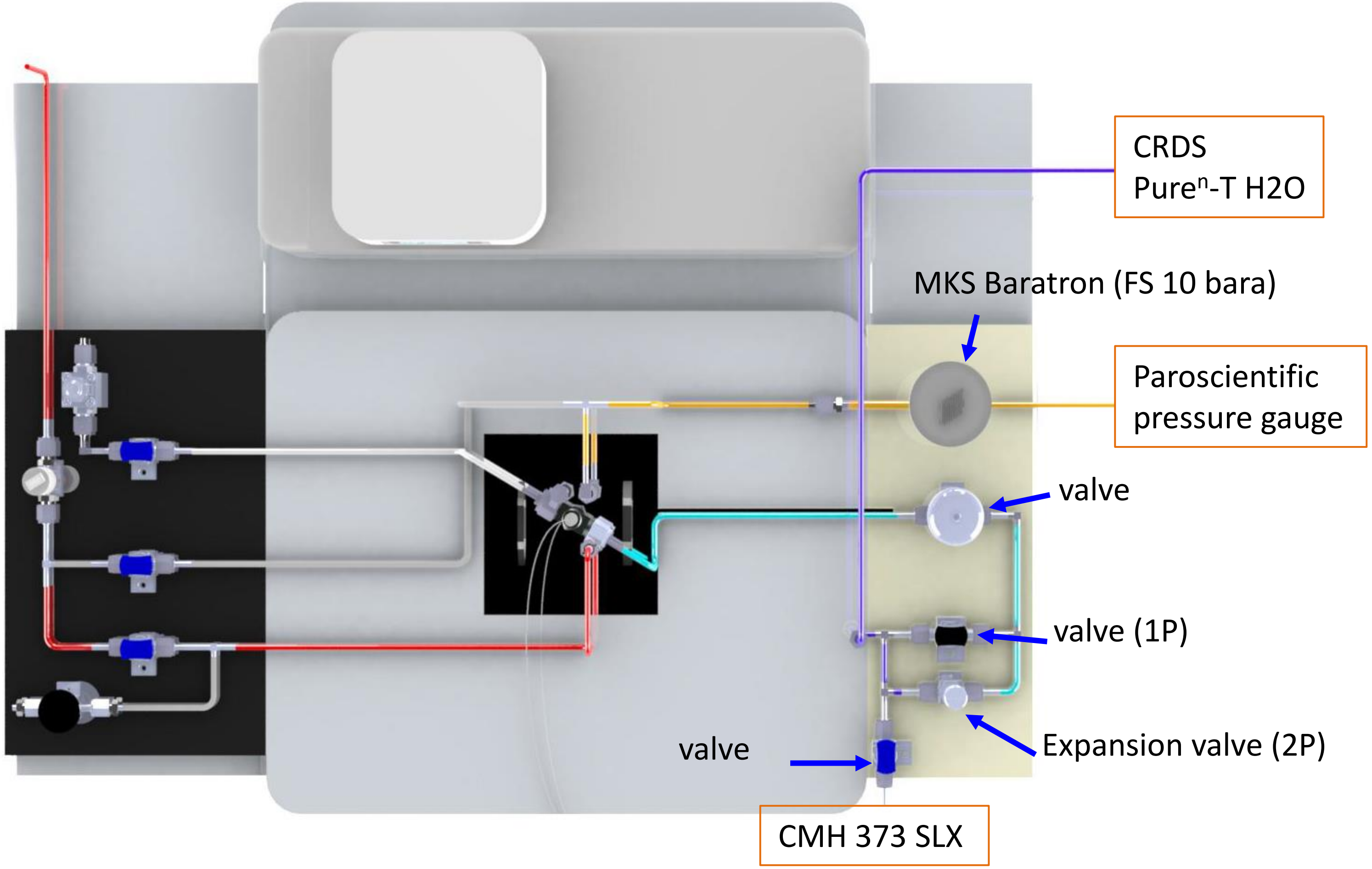
LFP HUMIDITY GENERATOR–Mark 2

RANGE EXPANSION

- 2-pressure, single-pass humidity generator
- **Frost-point temperature between -105 °C and -20 °C**
- **Water vapour mole fraction between 5 ppb_v and 1038 ppm_v @1000 hPa**
- Pressure: 200 hPa to 6800 hPa
- Carrier gas: Nitrogen, Argon *(to be done)*

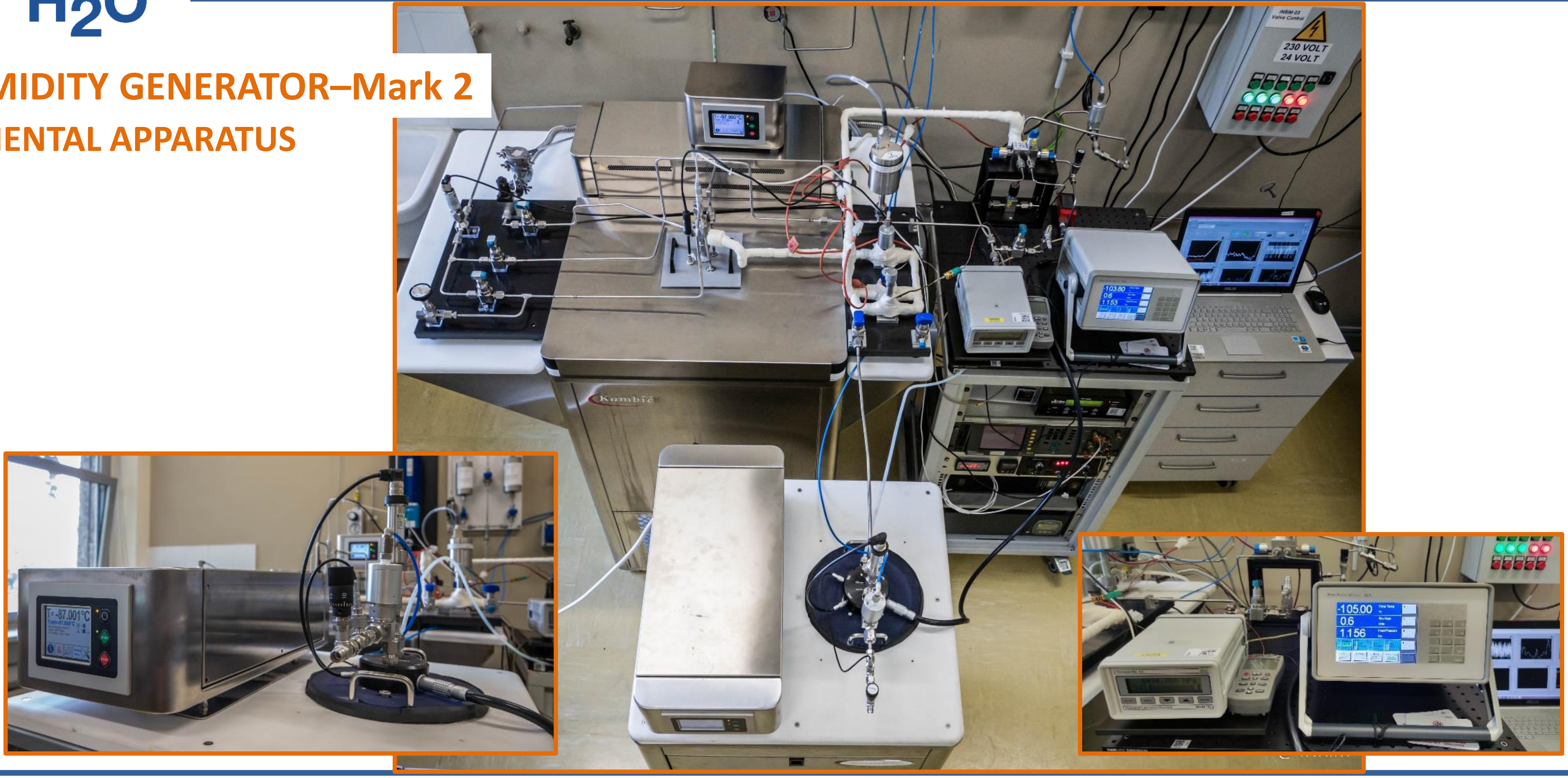
New trace water analysers:

- CMH: MBW 373-SLX (-110 °C < T_{fp}< 20 °C; 50 kPa < P < 250 kPa)
- CRDS: Photonics Technologies Pure^n-T H2O (0-20 ppm in N_2, LDL 200 ppt)



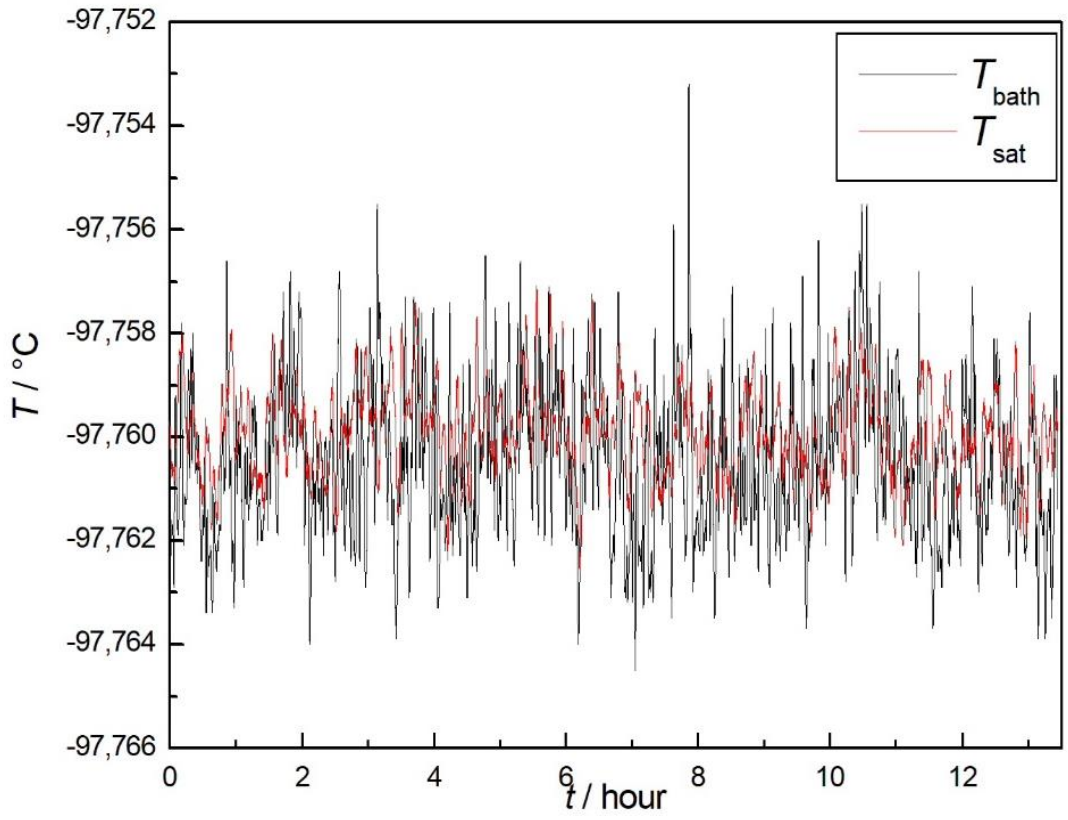
Activity 2.1.1
INRIM

LFP HUMIDITY GENERATOR–Mark 2
EXPERIMENTAL APPARATUS

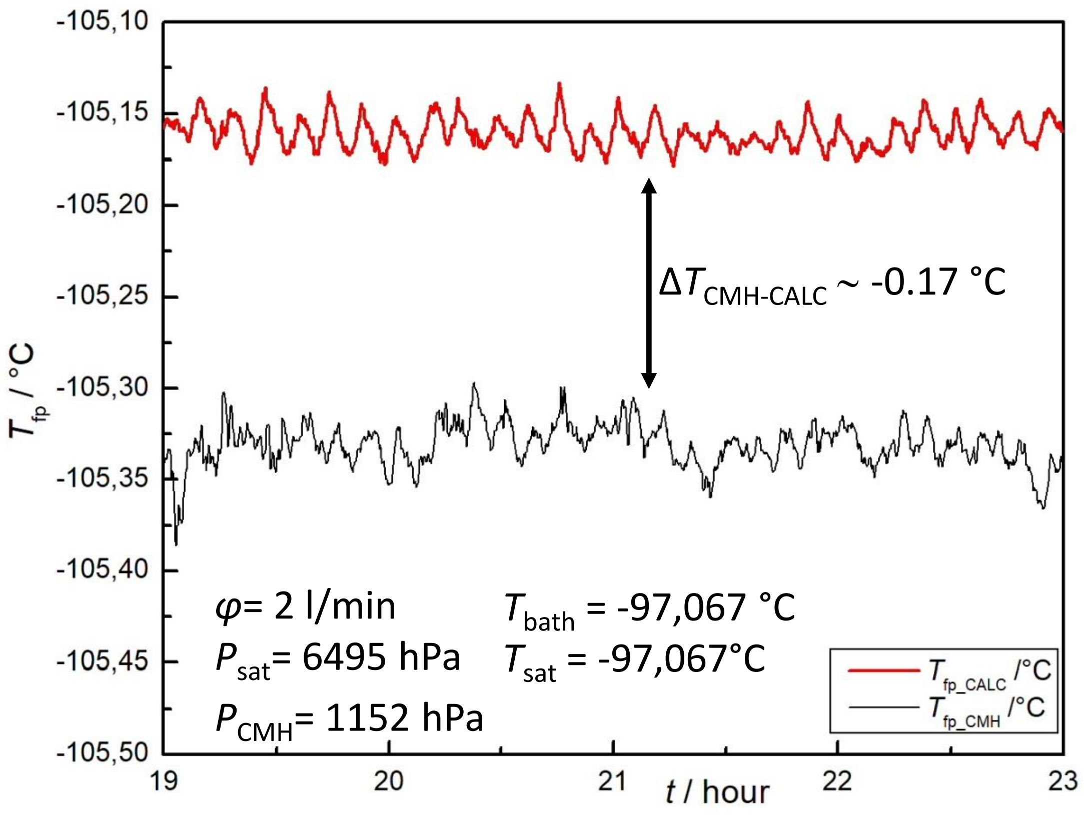


CHARACTERISATION OF THE LFP HUMIDITY GENERATOR – Mark 2

Temperature stability of the LFP humidity generator.

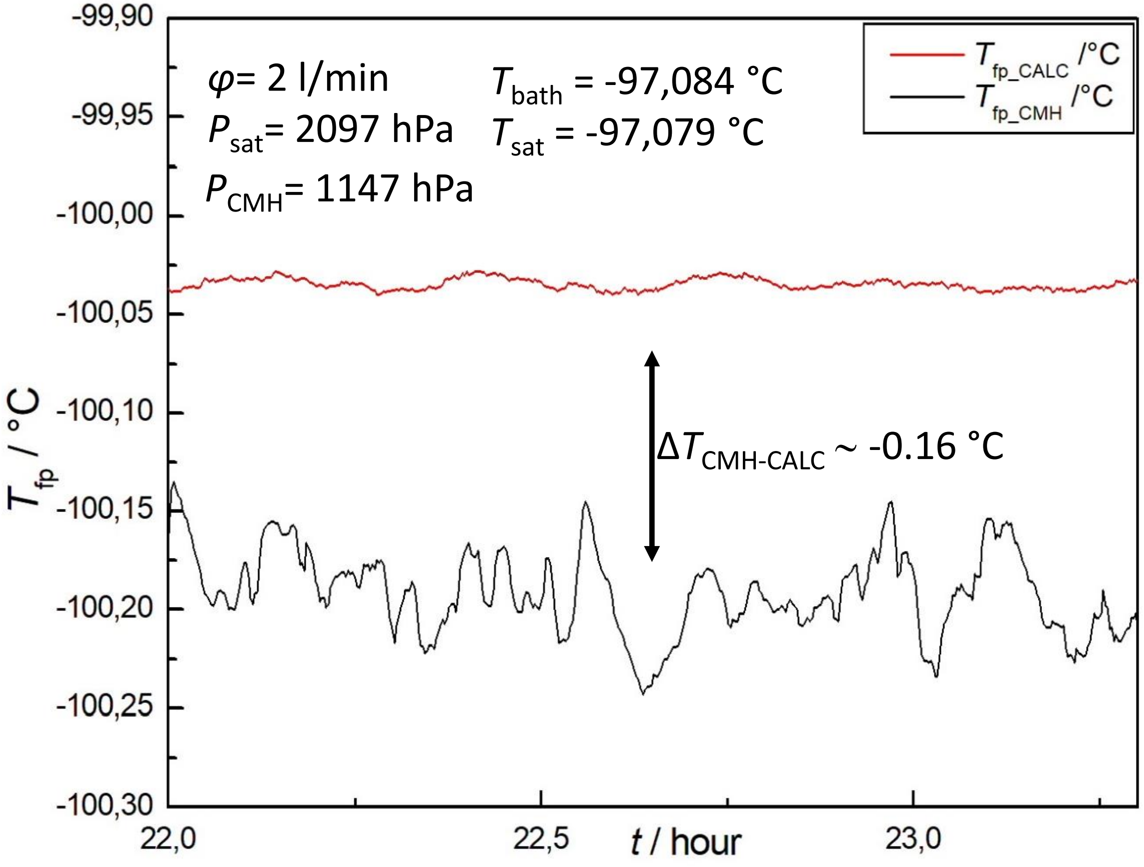


Experimental measurements at $T_{fp} \sim -105$ °C.

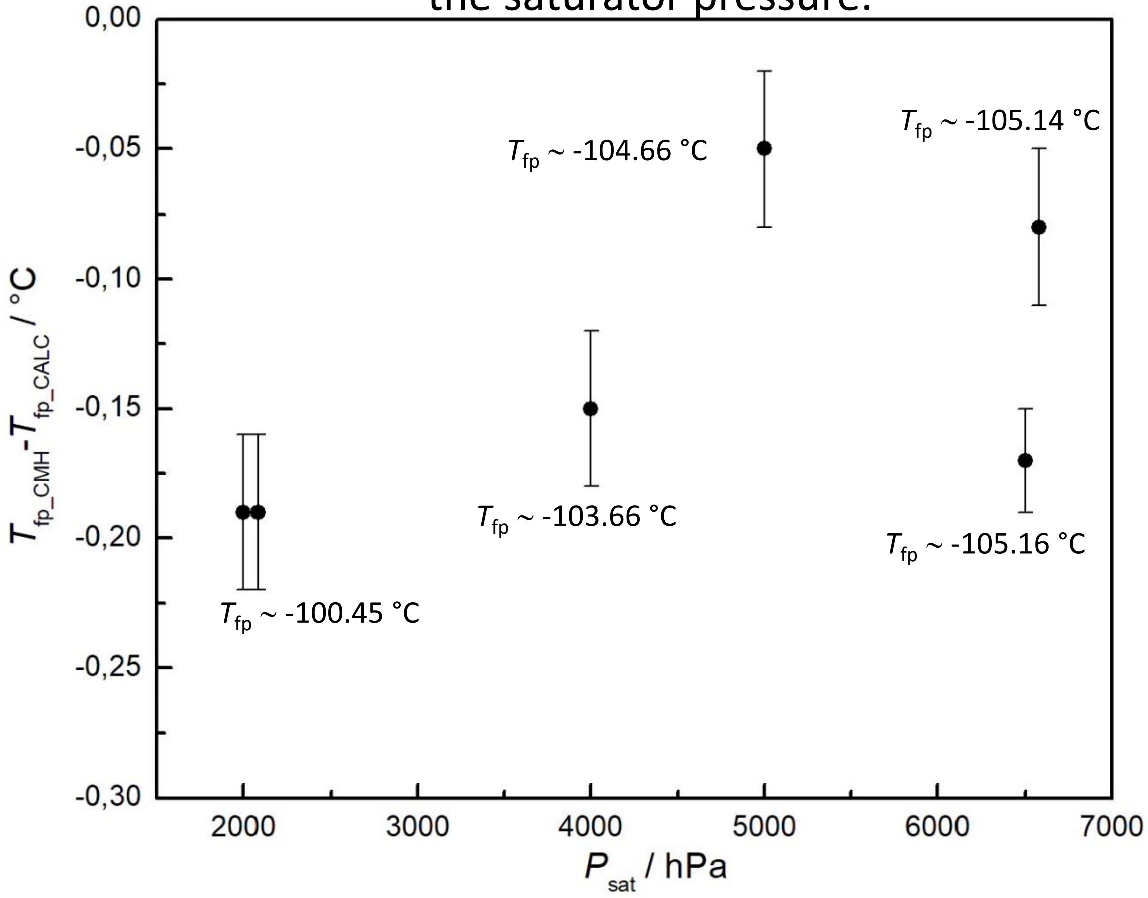


CHARACTERISATION OF THE LFP HUMIDITY GENERATOR – Mark 2

Experimental measurements at T_{fp} ~ -100 °C.



Efficiency of the LFP humidity generator vs the saturator pressure.

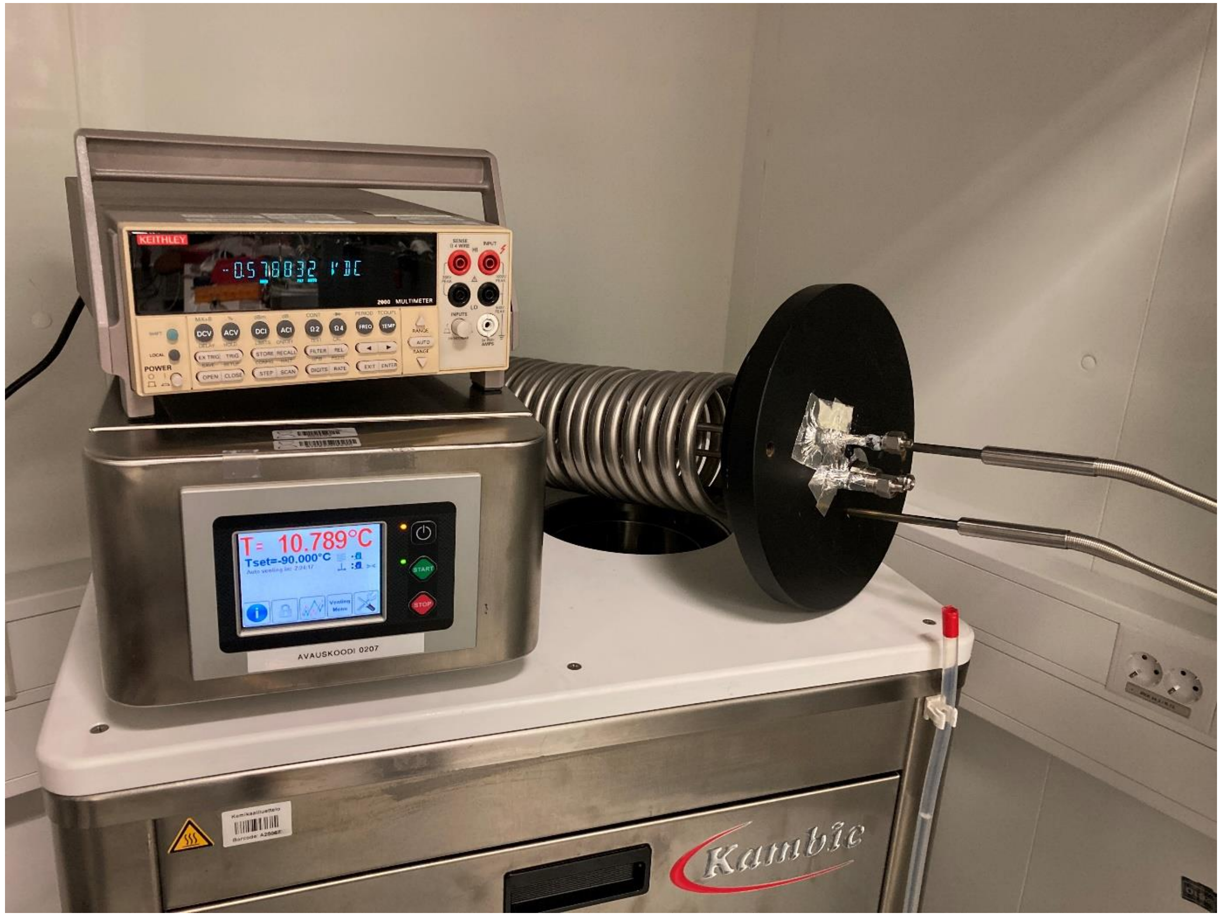


Humidity generator - VTT

- The generator was operating at the beginning of the project.
- The thermostatic bath had some malfunctioning and was transported for repairment.
- We finally got the thermostatic bath repaired and tested.

We look forward to reduce the uncertainty levels:

- Adsorption/desorption contributes to the uncertainty budget by 27%
- Temperature gradient contributes by 4%.
- Our target is to shrink the uncertainty budget possibly by 20-25%



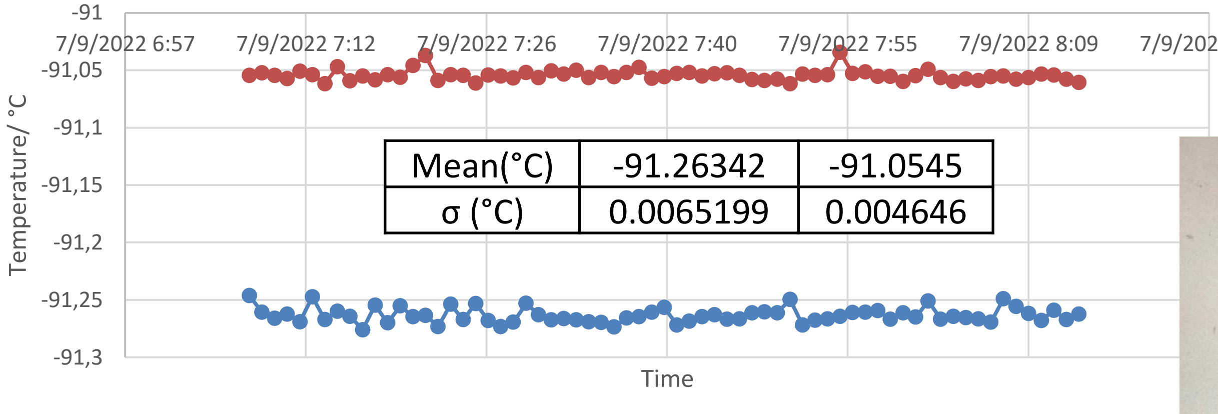
Characterization of the thermostatic bath

- It went down to -94.35 °C with setpoint -95 and the standard deviation in 2 hour measurement was 6 mK.

- Stability was tested down to -90 °C and also lifted from original immersion depth, which was 20 cm by:

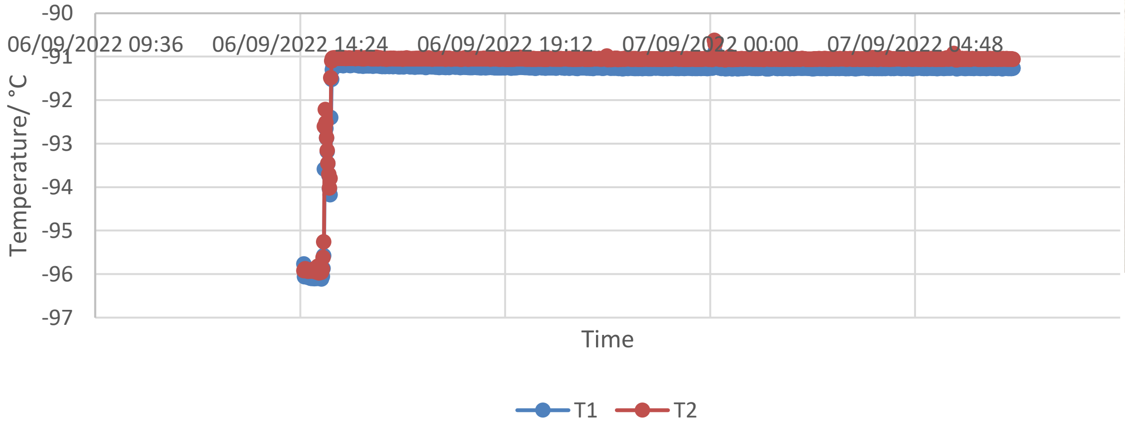
  0 cm: T = -89.393 °C, σ= 8 mK
  +2 cm: T = -89.392 °C, σ= 8 mK
  +6 cm: T = -89.367 °C, σ= 7 mK

- Close to the specification ± 0.005 @ - 90 °C

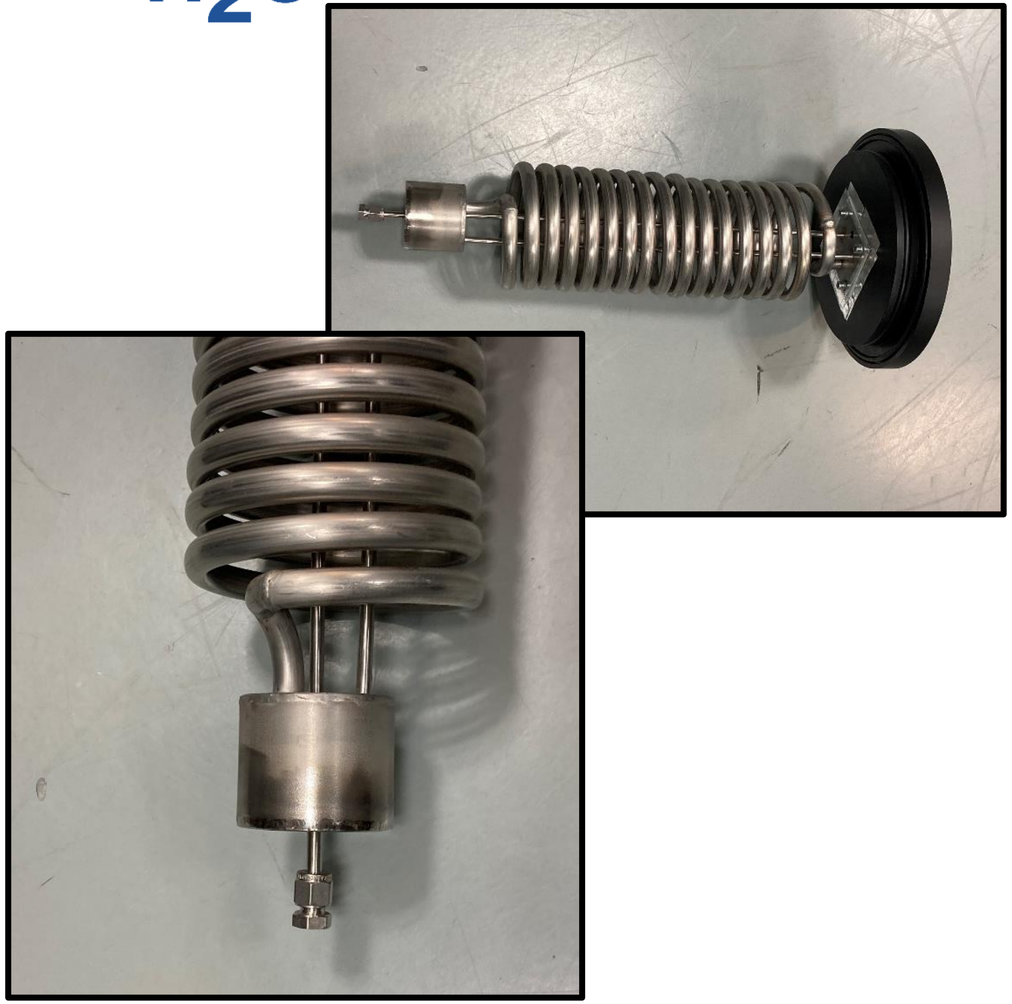


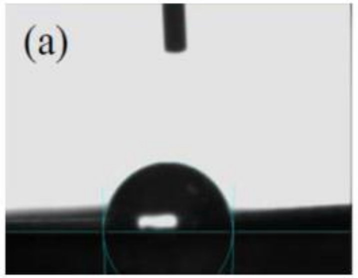
Mean(°C)	-91.26342	-91.0545
σ (°C)	0.0065199	0.004646

Immersion depth appr. 20-25 cm, T1 in center and T2 appr. 2 cm away from T1

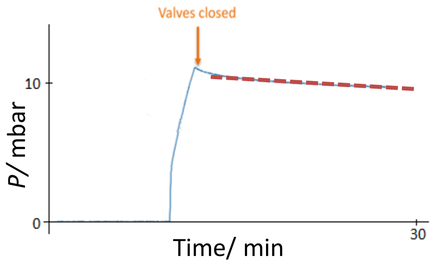


Reduction of the water adsorption/desorption





Droplet of water on highly polished SS 316L

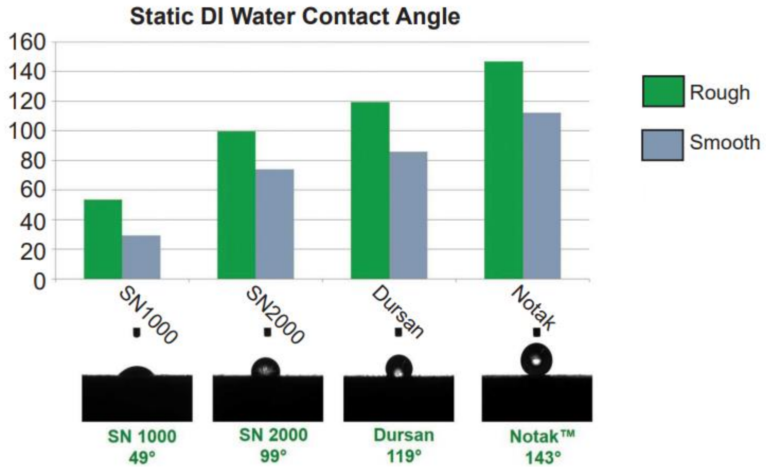


Pressure stabilization time is reduced significantly by introducing Dursan coating

Coating techniques based on Chemical Vapor Deposition (CVD) :

NON-WETTING

SilcoNert 2000 doubles the hydrophobicity of stainless steel and is commonly specified in moisture analyzer applications.



C2.a Task 2.1: Development of primary humidity standards for trace water vapour in an increased range of gas matrices

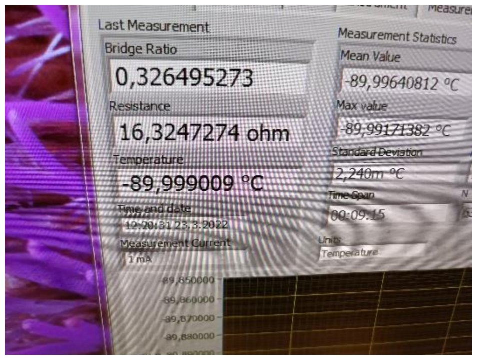
The aim of this task is to develop primary humidity standards for ultra-trace water vapour in an increased range of gas matrices (nitrogen, air, argon and hydrogen) based on a range of principles providing traceability through different routes.

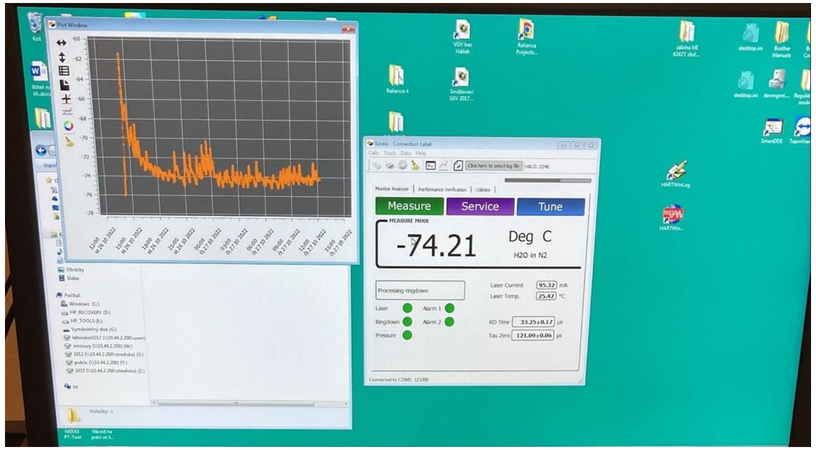
	Activity number	Activity description	Partners (Lead in bold)	
12/2022	A2.1.2 M18	CMI, INTA and UL will **upgrade their saturation-based generators** to produce humid gas mixtures in nitrogen and argon to extend the lower limit of reference frost-point temperatures **to -90 °C** and at **pressures up to 1 MPa and above**, with standard uncertainty of 0.25 °C at -90 °C. Only for INTA the pressure will go to 0.5 MPa.	**CMI**, INTA, UL	Measurements running
12/2023	A2.1.6 M30	INRIM, VTT, CMI, INTA, UL, PTB, MBW, VSL, and CETIAT using the results from A2.1.1 to A2.1.5 will write a summary report on the development of the trace water vapour standards describing the range and uncertainty achievable and the gas species in which reference humidity values can be generated.	**INRIM**, VTT, CMI, INTA, UL, PTB, MBW, VSL, CETIAT	inactive
	A2.1.7 M30	INRIM, VTT, CMI, INTA, UL, PTB, MBW, VSL, and CETIAT will review the report from A2.1.6 and will send it to the coordinator. Once the report has been agreed by the consortium, the coordinator on behalf of INRIM, VTT, CMI, INTA, UL, PTB, MBW, VSL, and CETIAT will then submit it to EURAMET as **D3**: *'Report on the development of primary trace water vapour standards describing the range, the estimated uncertainty and the gas species in which reference values can be generated with a target fraction range from 5 ppm to 5 ppb (-65 °C to -105 °C) with relative standard uncertainty less than 3 % to 8 % in selected gas matrices at pressures up to 1 MPa'.*	**INRIM**, VTT, CMI, INTA, UL, PTB, MBW, VSL, CETIAT	

A2.1.2

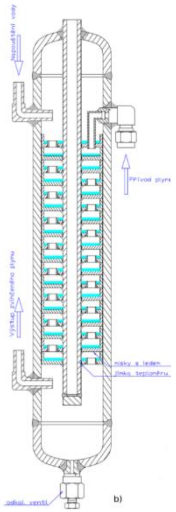
upgrade of saturation-based generator to produce humid gas mixtures in nitrogen and argon to extend the lower limit of reference frost-point temperatures to -90 °C and at pressures up to 1 MPa and above, with standard uncertainty of 0.25 °C at -90 °C

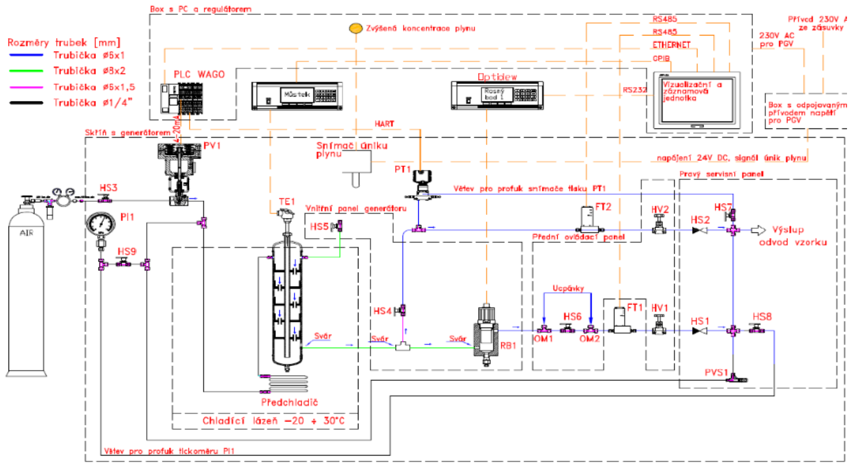
- Cryogenic bath and SPRTs prepared and characterised, implemented into an already existing system
- Validation at -90 $°C_{fp}$: measurements are running (efficiency of saturation, stability, precision, uncertainty,…)





- **Primary humidity generator,** 1P1T type, thermodynamic saturation-based principle, in Prague:
    - Pressure: 15 MPa max.
    - Humidity range: (-80 to 30) $°C_{dp/fp}$
    - Gas matrix: Air, N_2, Ar, CH_4, natural gas
    - Flow rate: up to approx. 2 L_N/min
    - ***U* (*k*=2)** from -80 $°C_{fp}$ to -30 $°C_{fp}$:
        - ✓ at **1 MPa**: 0.11-0.23 °C
        - ✓ at **0.1 MPa**: 0.09-0.15 °C or less





Activity 2.2.2
New devices - CMI

Kambič Calibration bath OB-22/2 ULT to -90 °C…

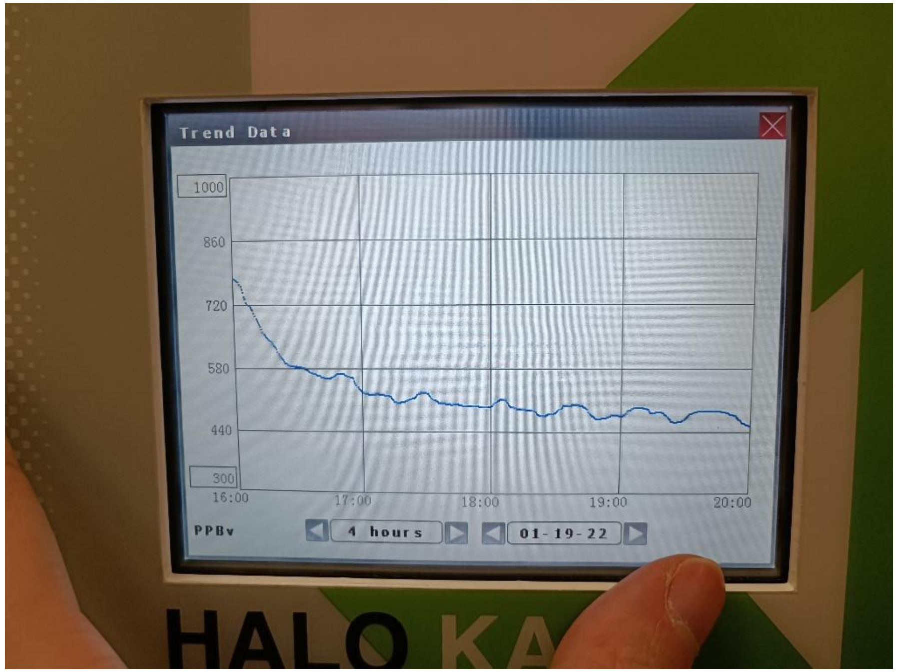
Thermometry bridge MI 6242T + resistance etalon
- improved temperature measurement precision

New SPRT glass temperature resistance probe…

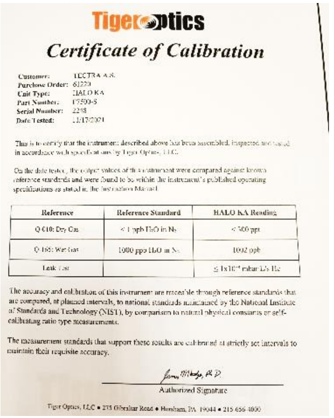
Thermodynamic saturator (expected maintaining function without modification)

Activity 2.2.2
New devices - CMI

New fraction humidity analyzer at CMI:
Tiger Optics, HALO KA H_2O – laser absorption CRDS hygrometer



tracebility (NIST)


TigerOptics

Certificate of Calibration

Reference	Reference Standard	HALO KA Reading

Authorized Signature

SW

Activity 2.2.2
New devices - CMI

New fraction humidity analyzer at CMI:
Tiger Optics, HALO KA H_2O

HALO KA H_2O
Ultra-High Purity Gas Analyzer

Performance	
Operating range	See table on next page
Detection limit (LDL, 3σ/24h)	See table on next page
Precision (1σ, greater of)	± 0.75% or 1/3 of LDL
Accuracy (greater of)	± 4% or LDL
Speed of response	< 2 minutes to 95%*
Environmental conditions	10°C to 40°C
	30% to 80% RH (non-condensing)
Storage temperature	-10°C to 50°C
Gas Handling System and Conditions	
Wetted materials	316L stainless steel
	(corrosive gas version optional)
	10 Ra surface finish
Gas connections	1/4" male VCR inlet and outlet
Leak tested to	1 x 10^{-9} mbar l / sec
Inlet pressure	10 – 125 psig (1.7 – 9.6 bara)
Flow rate	0.05 – 1.8 slpm
Sample gases	Most inert, toxic, passive
	and corrosive matrices
Gas temperature	Up to 60°C

Dimensions	H x W x D [in (mm)]
Standard sensor	8.73 x 8.57 x 23.6 (222 x 218 x 599)
Sensor rack	8.73 x 19.0 x 23.6 (222 x 483 x 599)
(fits up to two sensors)	
Weight	
Standard sensor	28 lbs (12.7 kg)
Electrical and Interfaces	
Platform	Max series analyzer
Alarm indicators	2 user programmable
	1 system fault
	Form C relays
Power requirements	90 – 240 VAC, 50/60 Hz
Power consumption	40 Watts max.
Signal output	Isolated 4–20 mA per sensor
User interfaces	5.7" LCD touchscreen
	10/100 Base-T Ethernet
	USB, RS-232, RS-485
	Modbus TCP (optional)
Data storage	Internal or external flash drive
Certification	CE Mark

	Performance, H_2O:	Range	LDL (3σ)	Precision (1σ) @ zero
INERT/ PASSIVE GASES	In Nitrogen	0 – 20 ppm	300 ppt	100 ppt
	In Helium	0 – 4 ppm	100 ppt	20 ppt
	In Argon	0 – 9 ppm	130 ppt	45 ppt
	In Hydrogen	0 – 16 ppm	200 ppt	70 ppt
	In Deuterium ($^2H_2$)	0 – 14 ppm	900 ppt	300 ppt
OXYGENATED GASES	In Oxygen	0 – 10 ppm	150 ppt	50 ppt
	In Clean Dry Air (CDA)	0 – 18 ppm	300 ppt	100 ppt
	In CO	0 – 24 ppm	600 ppt	200 ppt
	In CO_2	0 – 25 ppm	800 ppt	300 ppt
	In COS	0 – 23 ppm	4 ppb	1.4 ppb
RARE GASES	In Neon	0 – 5 ppm	100 ppt	30 ppt
	In Krypton	0 – 11 ppm	160 ppt	60 ppt
	In Xenon	0 – 13 ppm	250 ppt	90 ppt
COR-ROSIVE GASES	In Cl_2*	0 – 25 ppm	650 ppt	220 ppt
	In HCl†	0 – 50 ppm	1200 ppt	400 ppt
	In HBr*	0 – 50 ppm	12 ppb	4 ppb
FLUORINATED GASES	In SF_6	0 – 15 ppm	400 ppt	140 ppt
	In NF_3	0 – 20 ppm	600 ppt	200 ppt
	In CF_4	0 – 15 ppm	800 ppt	300 ppt
	In C_2F_6	0 – 15 ppm	1200 ppt	400 ppt
	In C_3F_8	0 – 20 ppm	1200 ppt	400 ppt
	In C_4F_6	0 – 25 ppm	150 ppb	50 ppb
	In C_4F_8	0 – 20 ppm	1200 ppt	400 ppt
	In C_5F_8	0 – 32 ppm	8 ppb	3 ppb
HY-DRIDE GASES	In 1% GeH_4/99% H_2 mixture	0 – 16 ppm	7 ppb	2.5 ppb
	In 10% GeH_4/90% H_2 mixture	0 – 16 ppm	35 ppb	12 ppb

*Corrosive gas version required
†Corrosive gas version recommended for H_2O concentration that could exceed 1 ppm

Contact us for additional analytes and matrices.
U.S. Patent # 7,277,177

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Made in U.S.A.

Tiger Optics
A Process Insights Company
3/2021

Activity 2.1.2
INTA

- **Task 2.1: Development of primary humidity standards for trace water vapour in an increased range of gas matrices**

A2.1.2 **M18**	**Upgrade their saturation-based generators to extend the lower limit of reference frost-point temperatures to -90 °C and at pressures up to 0.5 MPa for INTA with standard uncertainty of 0.25 °C at -90 °C.**	**CMI, INTA, UL**

PERFORMED:

✓ **Recalibration of pressure and temperature sensors of 2-P based on saturation standard humidity generator.**

✓ **Maintenance and checking of auxiliar systems:**

Nitrogen → SAES Getter purifiers

Compressed air system free of CO_2

- **Task 2.1: Development of primary humidity standards for trace water vapour in an increased range of gas matrices**

A2.1.2 **M18**	**Upgrade their saturation-based generators to extend the lower limit of reference frost-point temperatures to -90 °C and at pressures up to 0.5 MPa for INTA with standard uncertainty of 0.25 °C at -90 °C.**	**CMI, INTA, UL**

Water Cooling System used is **DAMAGED**

- Maintenance dossier was approved.
- Waiting for successful bidding company come to repair the water cooler

ACTUAL STATUS: Experimental measurements **not started** for reasons beyond the laboratory.

Activity 2.1.2
UL

A2.1.2 M18	CMI, INTA and UL will **upgrade their saturation-based generators** to extend the lower limit of reference frost-point temperatures to **-90 °C** and at pressures up to **1 MPa** and above (INTA to 0.5 MPa) with standard uncertainty of 0.25 °C at -90 °C. Such trace water generators in nitrogen and argon will perform/support the investigation of water vapour enhancement factor in Task 2.2. Participation in the pilot study described in Task 1.3 requires these standards to be available.	**CMI**, INTA, UL

The existing generator

- generator designed for frost point -95 °C at atmospheric pressure – single-pass

- the weak link for higher pressure was the saturator –
withstands higher pressures, but not designed for (safety, swelling, cross-channel leakage)

A2.1.2 M18	CMI, INTA and UL will **upgrade their saturation-based generators** to extend the lower limit of reference frost-point temperatures to **-90 °C** and at pressures up to **1 MPa** and above (INTA to 0.5 MPa) with standard uncertainty of 0.25 °C at -90 °C. Such trace water generators in nitrogen and argon will perform/support the investigation of water vapour enhancement factor in Task 2.2. Participation in the pilot study described in Task 1.3 requires these standards to be available.	**CMI**, INTA, UL

The upgrade

- the new saturator designed and manufactured for >1 Mpa.
- reinforced housing,… (Directive 2014/29/EU)
- pressure regulation redesigned

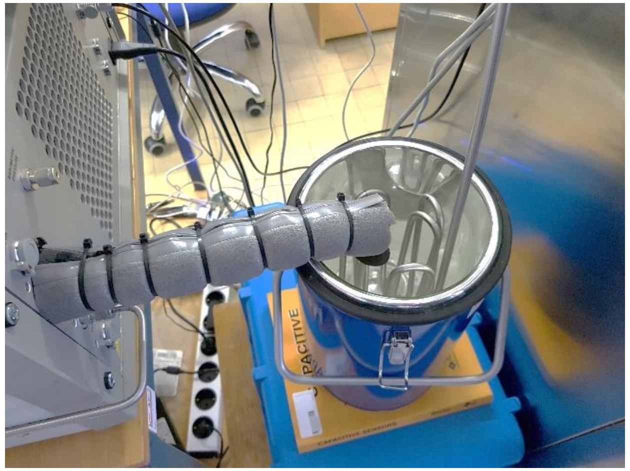
A2.1.2 M18	CMI, INTA and UL will **upgrade their saturation-based generators** to extend the lower limit of reference frost-point temperatures to **-90 °C** and at pressures up to **1 MPa** and above (INTA to 0.5 MPa) with standard uncertainty of 0.25 °C at -90 °C. Such trace water generators in nitrogen and argon will perform/support the investigation of water vapour enhancement factor in Task 2.2. Participation in the pilot study described in Task 1.3 requires these standards to be available.	**CMI**, INTA, UL

Issues

- saturator prototype - not sufficient surface finish -> delay
- delay also due to staff issues (key person left, but still helps)
- expected to finish by M22 (to lineup with task 2.2.2, due in M24)

Activity 2.1.2
UL

A2.1.2 M18	CMI, INTA and UL will **upgrade their saturation-based generators** to extend the lower limit of reference frost-point temperatures to **-90 °C** and at pressures up to **1 MPa** and above (INTA to 0.5 MPa) with standard uncertainty of 0.25 °C at -90 °C. Such trace water generators in nitrogen and argon will perform/support the investigation of water vapour enhancement factor in Task 2.2. Participation in the pilot study described in Task 1.3 requires these standards to be available.	**CMI**, INTA, UL



Expected issues with instruments

- LXHX issues below -80 °C
- unsuccessful bid for SLX
- planned retry (SLX, LX, …)
- additional requirements for enh. factor measurements

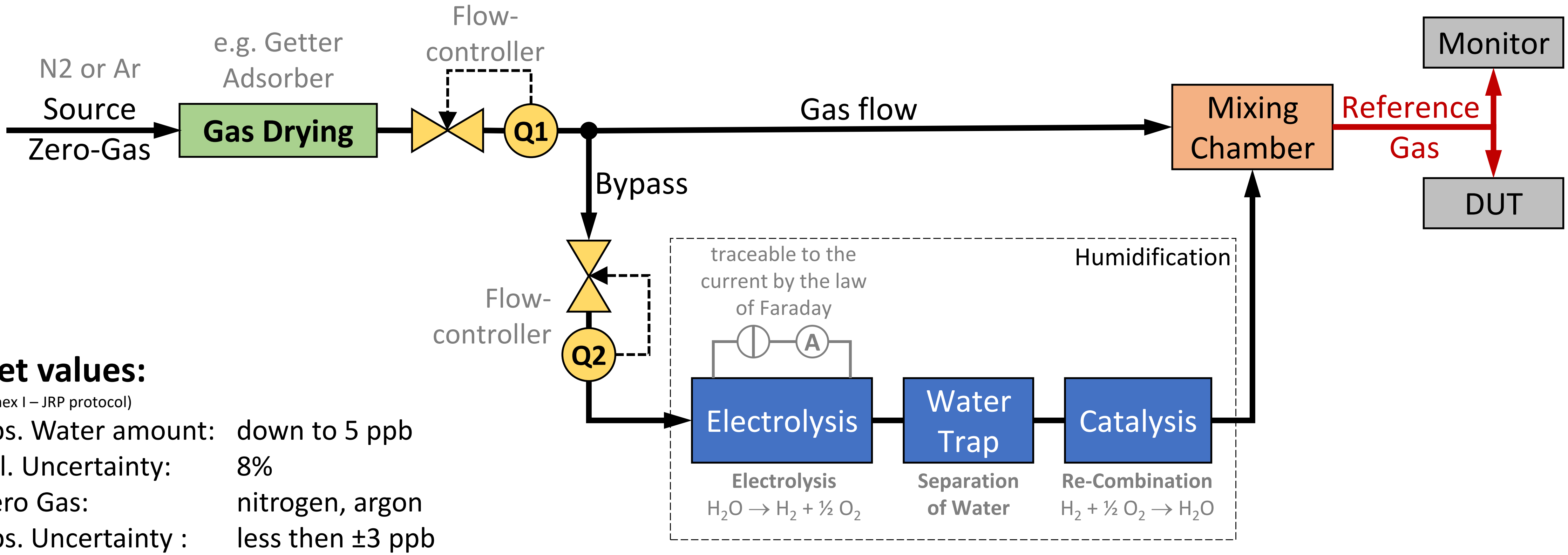
PTB Tasks in WP2

- **Task 2.1.3 – M30 (Development/Testing):**
  Development of a coulometric principal standard to generate water vapour in nitrogen and argon. Tests of selected instruments with the generator.
  (**PTB**, MBW)

- **Task 2.1.6 – M30 (Report):**
  Summary report on the development of the trace water vapour standards.
  (**INRIM**, VTT, CMI, INTA, UL, **PTB**, MBW, VSL, CETIAT)

- **Task 2.1.7 – M30 (Review):**
  Review of the report (A2.1.6) and send it to the coordinator.
  (**INRIM**, VTT, CMI, INTA, UL, **PTB**, MBW, VSL, CETIAT)

Basic setup of the Coulometric Trace Water Generator (CTWG)



Target values:

(from Annex I – JRP protocol)

- abs. Water amount: down to 5 ppb
  rel. Uncertainty: 8%
- Zero Gas: nitrogen, argon
  abs. Uncertainty : less then ±3 ppb

Based on the idea of: P. Mackrodt, "A New Attempt on a Coulometric Trace Humidity Generator", Int J Thermophys 33, 1520–1535 (2012). DOI 10.1007/s10765-012-1348-0

Activity 2.1.3
Survey of current and next steps - PTB

Finished

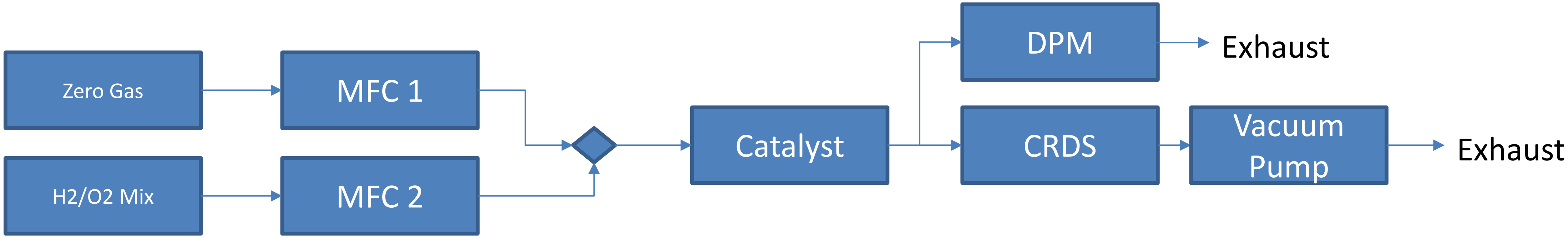
- Development of overall Coulometric Trace Water Generator (**CTWG**) concept
- Initial analyses of catalysts for water synthesis
  - Equation: $2\ H_2 + O_2 \rightarrow 2\ H_2O$
- Initial tests of commercial and newly developed gas purification systems
  - Detection: high sensitivity H_2O Cavity Ring Down Spectroscopy (**CRDS**)

Steps in progress

- In-depth analysis of catalysts
  - commercial product vs. new designs
- In-depth investigation of gas purification systems
- Test of electrolysis cell
  - reported, newly developed and alternative designs
- Acquisition of hardware
  - Gas purification (Cooling Trap, Gas Drying)
  - Electrolysis Cell

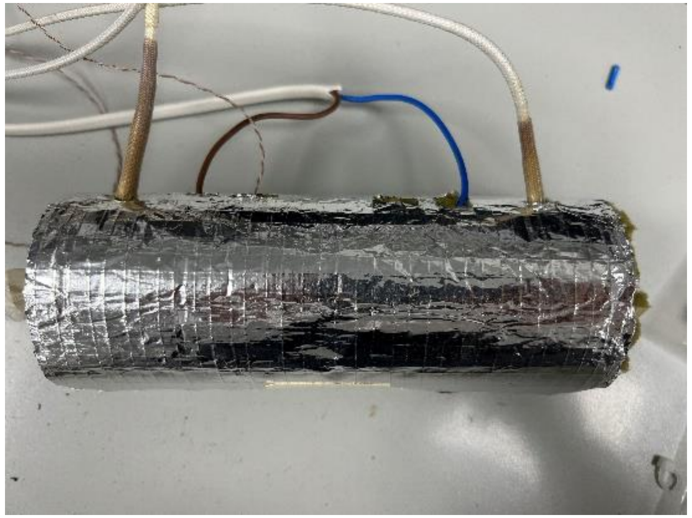
Schedule for major steps

Elaboration of final subcomponent design	**22/q1 23**
Acquisition of hardware (see above)	**ongoing**
Finalization of system design (system vs subcomponents)	**q2 23**
Commissioning and measurements	**until Nov 23**



Catalyst

- Active Material: Platinum
- Investigated 3 designs
  - Flow 3-5 ln/min
  - Environment: Standard RT and p
- Tested Range: approx. 500 ppb – 80 ppm



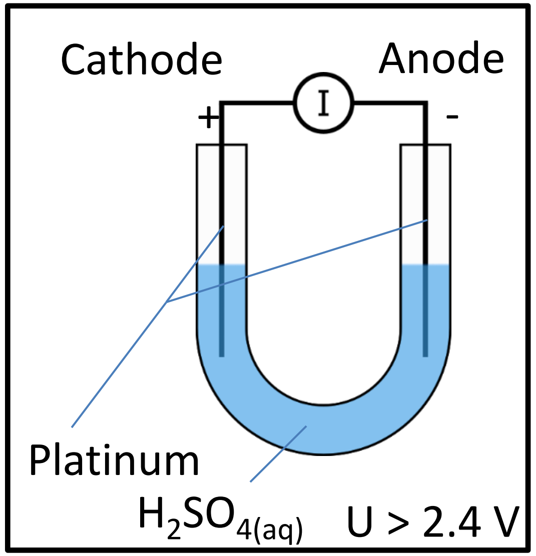
Activity 2.1.3
Electrolysis and Gas Purification - PTB

Electrolysis Cell

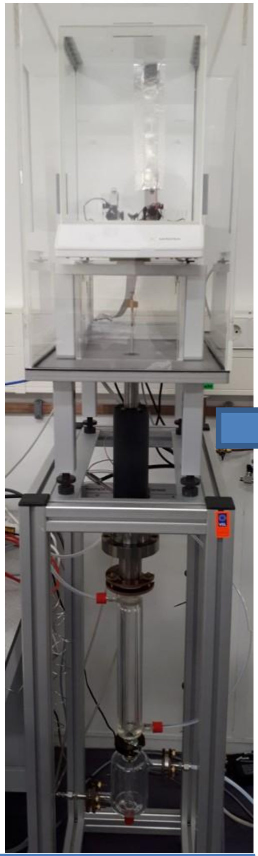
- Principle:
  - Platinum electrodes with aqueous acidic electrolyte
- Evaluation of design
  - old vs. new vs. commercial
- Performance Analysis of Cell

Gas Purification

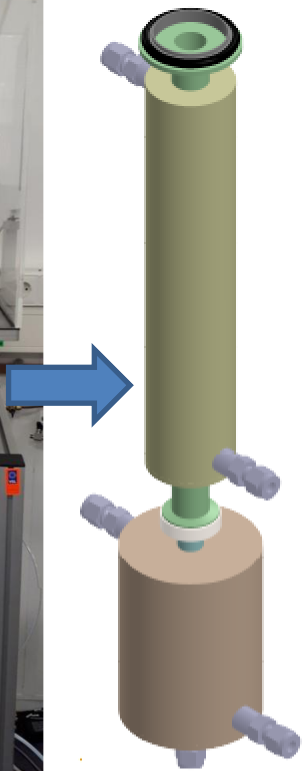
- Water Trap
  - Based on Cooling Trap
- Gas Drying
  - Study on enhancing system



Permeation system based on a passivated magnetic suspension balance - VSL



previous



design

Set up a permeation system based on a passivated magnetic suspension balance to generate primary standard of water amount fractions following ISO 6145-10 and ISO 6145-7.

Target range: in the range of 50 nmol/mol up to 5 µmol/mol

Matrix gases: N_2 and H_2

Initial steps taken:

1) **Completed design. External company manufactured metal chamber with less connections compared to glass chamber**
2) **Ordered new purifier**
3) **Started testing**

new chamber

- **CRDS analyzer Tiger Optics**

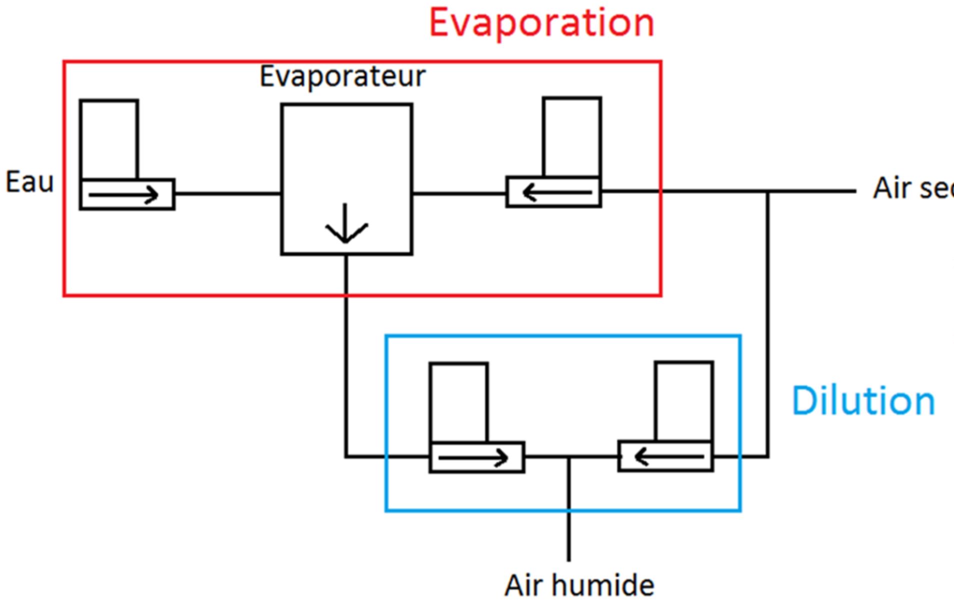
Analyzer broke down (June). Back in October. Repair $$$$$$

- **Permeation system**

- Water bath broke. Ordered a new one (February). Order disappeared from ordering system. Spare water bath installed. Also broke down. Made new order. Delivery delayed to November.
- Permeation system hardware 13 years old. Issues with operating. New hardware (electronics & PC) ordered and will be delivered in December.

Activity number	Activity description	Partners
A2.1.5 M18	CETIAT will upgrade its mixed flow generator in pressure, from 0.1 MPa up to 1 MPa, and in frost point temperature, from -85 °C down to -90 °C, possibly -95 °C, with a standard uncertainty of 0.25°C.	**CETIAT**

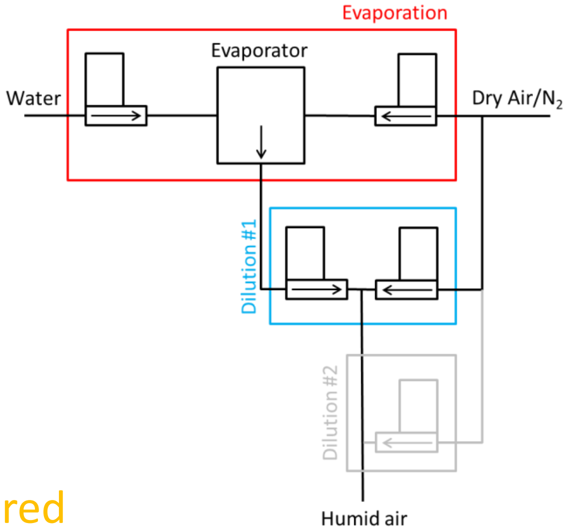
- Upgrade of the mixed flow generator / JRP METEOMET 2

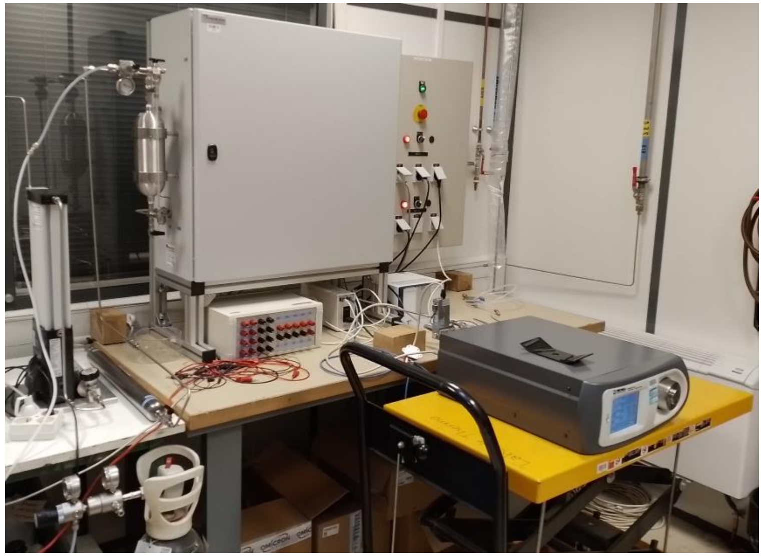


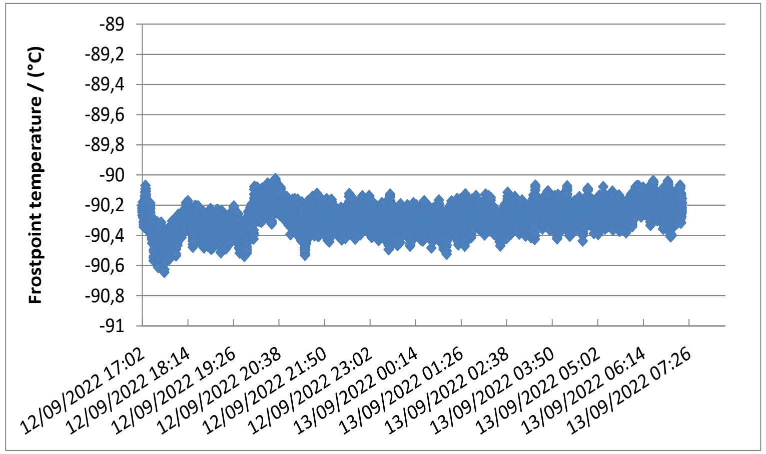
- $r_{evap} = \frac{m_{water}}{m_{dry\ air,MFC\ 1}} = \frac{\dot{m}_{water}}{\dot{m}_{dry\ air,MFC\ 1}}$
- $r_{dilu} = \frac{\dot{m}_{humid\ air,MFC\ 2} \cdot r_{evap}}{\dot{m}_{humid\ air,MFC\ 2} + \dot{m}_{dry\ air,MFC\ 3}}$
- from r_{dilu} to $\theta_{d/f}$
  - $x_v = r_{dilution} \cdot \frac{M_{air\ sec}}{M_{vapeur\ d'eau}}$
  - $e' = x_v \cdot p$
  - $e = \frac{e'}{f(p, t_{gelée})}$
  - $\theta_{d/f}$

D. Sonntag (EIT-90)

- Upgrade of the mixed flow generator
  - Pressure range from 40 kPa to 1000 kPa
    - Successful implementation
    - SI traceability of reference instruments
  - Frost point range
    - Upgrade down to -90 °C
      - Use of molecular sieve
    - Upgrade down to -95 °C
      - Additional dilution step is considered
  - Uncertainty $U_{k=2}$=0,35 °C
    - Uncertainty budget established
    - Validation to be done (ILC)

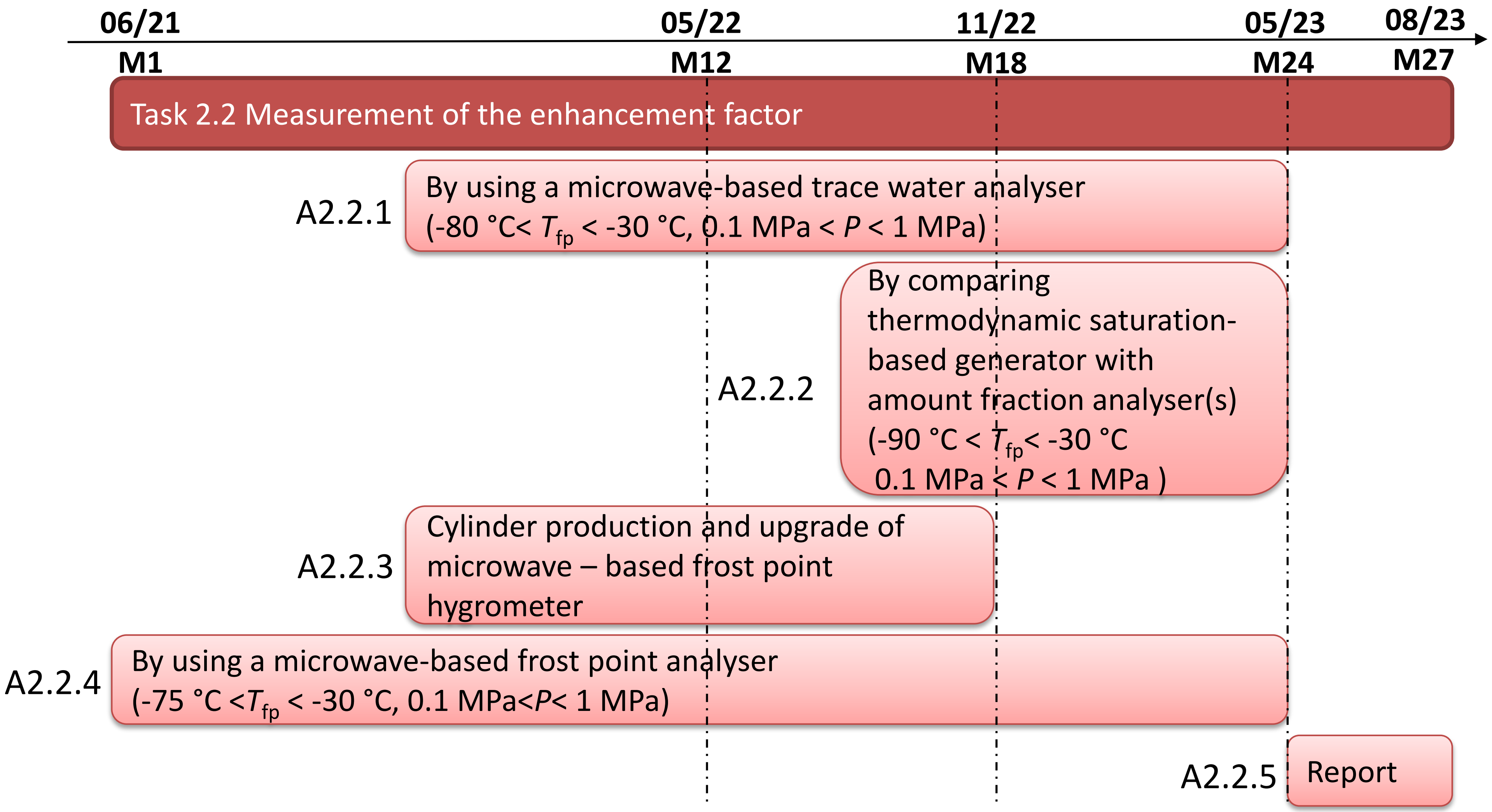






Task 2.2
Measurement of the enhancement factor in selected humid gas mixtures

Task 2.2: Activities



CNAM, contribution to the project (first 18 months):

- Conception of the new hygrometer (Activity A2.2.1)
- Coordination with CETIAT (Activity A2.2.1)
- Study of the equation of the system (Activity A2.2.1)

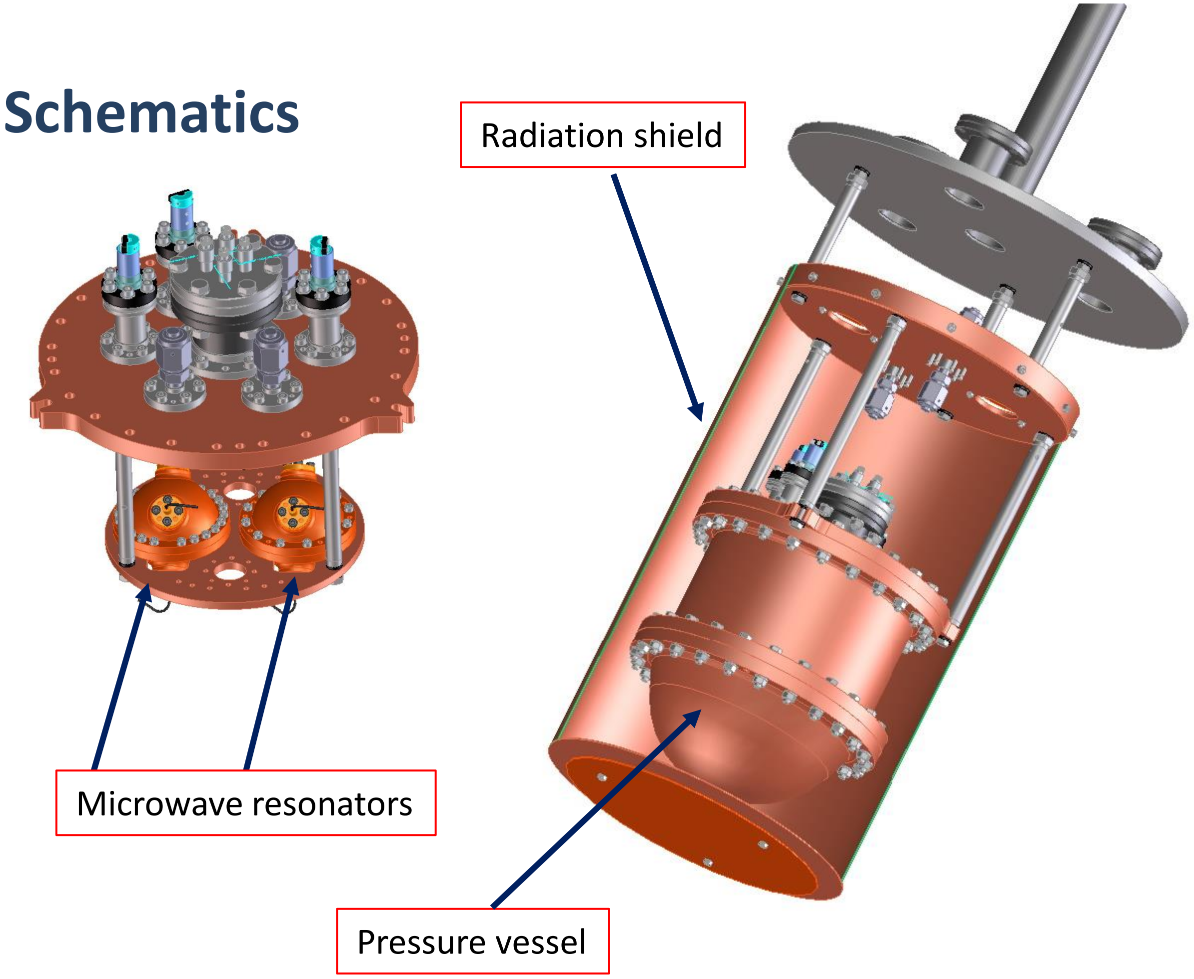
New hygrometer (activity A2.2.1)

Design of the new hygrometer system operating up to a pressure of 7-10 bar: we have completed the design of the new system.

The manufacturing procedure and the purchase process are slowed down at the administrative level.

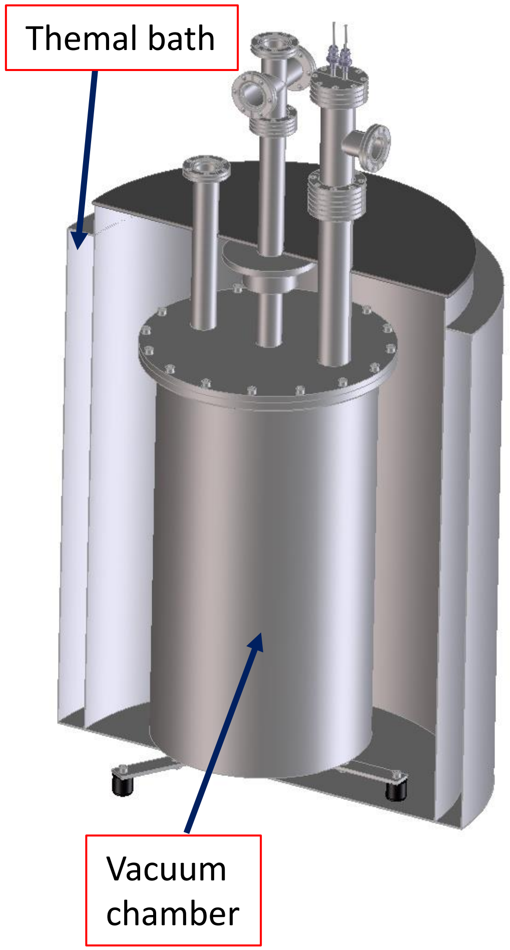
Possible risks: bureaucracy and shortage of raw materials (copper, aluminum) could lengthen manufacturing times by several months.

Schematics



Coordination with CETIAT (activity A2.2.1)

The partners CETIAT and CNAM are concerting the availability of the experimental equipment of the partnership of this project.



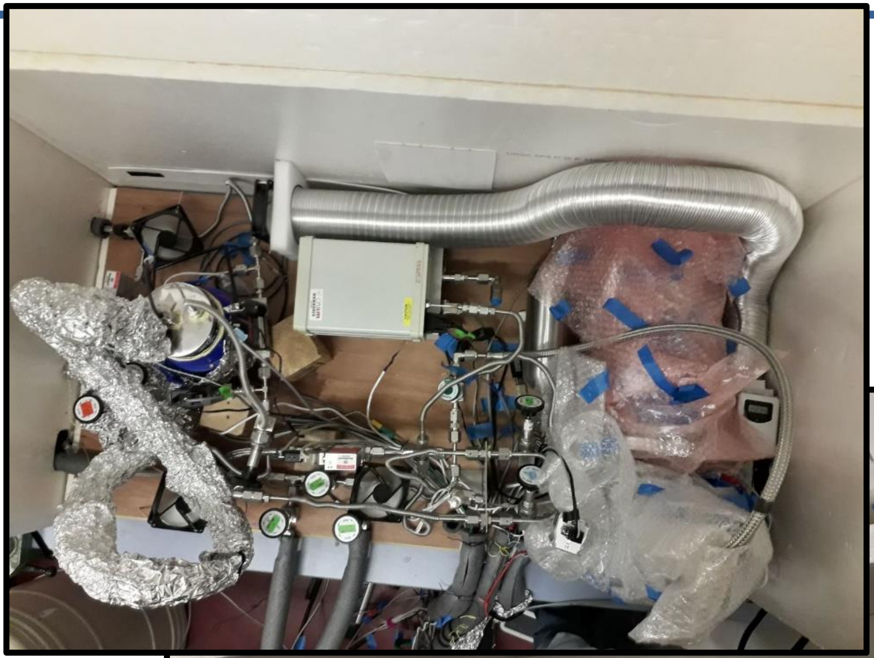
Activity 2.2.1
Old hygrometer – CNAM

Study of the equations of the system (activity A2.2.1)

CNAM has started to modify the actual experimental setup to perform preliminary measures: modification and improvement to perform from 1.2 bar to 1.9 bar.

Preliminary measures are in progress. Robustness test, modification of some components.

Actual pressure limit: 2 bar.



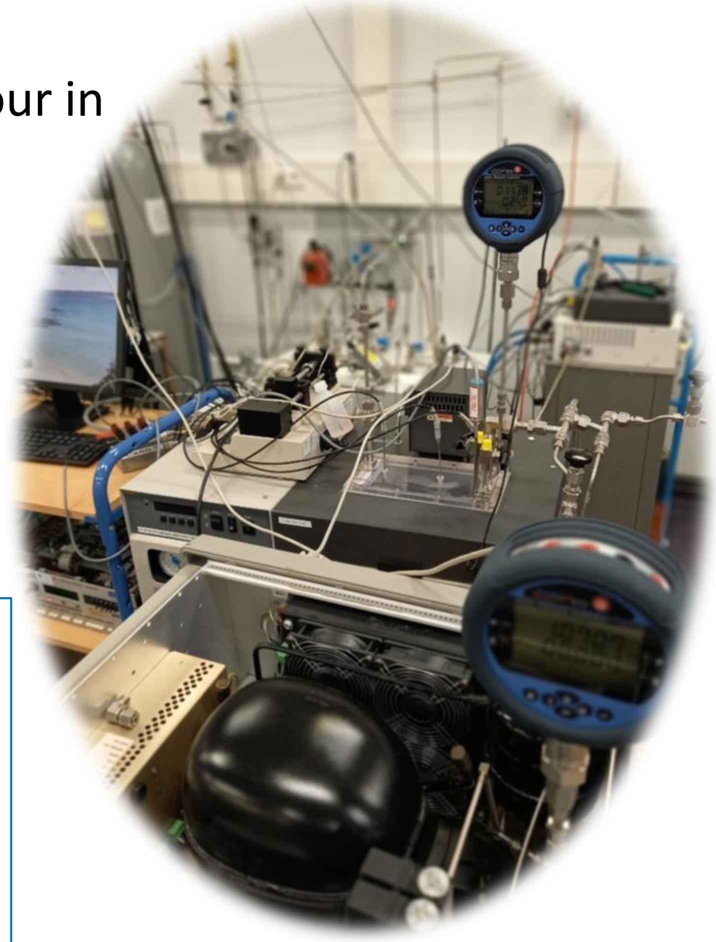
C2.b Task 2.2: Measurement of the enhancement factor in selected humid gas mixtures

The aim of this task is to improve the measurements available for water vapour enhancement factor in nitrogen, argon and hydrogen at selected temperatures and pressures, in the frost-point temperature range between -90 °C and -30 °C and pressure range from 0.1 MPa to above 1 MPa.

	Activity number	Activity description	Partners (Lead in bold)	
6/2023	A2.2.2 M24	CMI and UL, using the upgraded saturation-based generators from A2.1.2, will perform independent measurements of the enhancement of water vapour in **nitrogen and argon** in the frost-point temperature range between **-90 °C and -30 °C**. VSL, using its existing standard, will confirm the measurements to -80 °C at selected pressures from **0.1 MPa to above 1 MPa**. These independent measurements will evaluate the non-ideality of gas mixtures (i.e., enhancement factor) with trace amount of water by comparing humid gas mixtures generated by frost-point temperature standards with corresponding humidity quantities as measured by amount-of-substance fraction analyser(s).	**CMI**, VSL, UL	inactive
9/2023	A2.2.5 M27	CNAM, using the results from A2.2.1 to A2.2.4 will prepare a report stating the improved measurements for water vapour enhancement factor in nitrogen, argon and hydrogen at selected temperatures and pressures, in the frost-point temperature range between -90 °C and -30 °C and pressure range from 0.1 MPa to above 1 MPa. CNAM, CETIAT, CMI, VSL, UL, INTA, CEM, UVa will review the report and provide feedback.	**CNAM**, CETIAT, CMI, VSL, UL, INTA, CEM, UVa	inactive

Enhancement factors of nitrogen and argon - VSL

Perform measurements of the enhancement factors of water vapour in different carrier gasses.



Target frost point range: 500 ppb / -80 °C , 1 ppm / -75 °C, 10 ppm / -60 °C , 127 ppm / -40 °C, 376 ppm / -30 °C
Pressure range: 0.1, 0.2, 0.5, 0.7, 0.9, and 1 MPa.
Carrier gas: N_2 and Ar.

In progress:
~~**1) Training of scientist (ongoing)**~~
~~**2) Testing and revalidation of the two-pressure system**~~
4) Waiting on the repair of the ethanol bath.
3) Validation of system with the enhancement factors for air:
CMH pressure at saturator pressure and atmospheric pressure

Activity 2.2.3
CEM

Activity number	Activity description	Partners (Lead in bold)
A2.2.3 M18	CEM will produce cylinders containing static, pressurised humid gas mixtures in matrices of nitrogen, argon and hydrogen with amount fractions of water vapour down to 1 µmol mol^{-1}. The target standard uncertainty for the cylinders is 3 % of value. The gas cylinders will be used to investigate water vapour enhancement factor by the microwave-based method developed by UVa. **CEM, March 2022** **UVa and CEM agreed to start with H_2O in matrix N_2 mixture with concentration level of 500 µmol·mol^{-1}. Expected date of preparation of the first mixture by May 2022.** **CEM, 11th July 2022** **At the beginning of June CEM informed UVa about the delay on preparation of the proposed mixture because of shortage of staff and increased workload. Some calculation on how the mixture could be prepared have been done but the new expected date is still pending. End of activity is scheduled by November 2022.** **CEM, 26th October 2022** **The mixture proposed in March is not prepared. CEM confirms a delay in the achievement of the activity.** **New schedule: CEM proposes to UVa a 3 months period to get the mixture prepared and delivered. UVa agreed but has expressed concern about any further delay.**	**CEM**, UVa

Activity 2.2.3 - 2.2.4
UVa

A2.2.3 M24 A2.2.4 M18	UVa and INTA, using the upgraded saturation-based generator from A2.1.2 and upgraded microwave-based frost point hygrometer in A2.2.3, will perform measurements of the enhancement of water vapour in nitrogen, argon and hydrogen in the frost-point temperature range between -75 °C and -30 °C at selected pressures from 0.1 MPa to above 1 MPa. These measurements will evaluate the non-ideality of gas mixtures (i.e., enhancement factor) with trace amount of water by comparing humid gas mixtures generated by trace humidity standards (saturator-based generators) with corresponding humidity quantities as measured by amount-of-substance fraction analyser. CEM confirms a delay in the achievement of the activity. New schedule: CEM proposes to UVa a 3 months period to get the mixture prepared and delivered. UVa agreed but has expressed concern about any further delay.	**UVa,** INTA

- UVa designed and ordered the construction of a 4 cm diameter golden-plated quasi-spherical microwave resonator (QSMWR), 15 µm gold thickness. The new hygrometer is held in TermoCal UVa´s premises.
- The new QSMWR has been tested. Antennas have been tuned offering high quality resonant modes. Software has been upgraded and fully setup.
- The construction of a new thermostat for the new QSMWR is completed.
- INTA has recalibrated the temperature and pressure sensors of the frost-point two pressure-two temperature saturation-based generator, an upgraded THUNDER SCIENTIFIC 4500 model, this equipment is now in TermoCal. INTA has calibrated of the transfer standard dew point hygrometer, MBW, DP 30 model, this equipment is now in TermoCal.
- The integration of the hygrometer, thermostat, QSMWR, control and software is being undertaken.

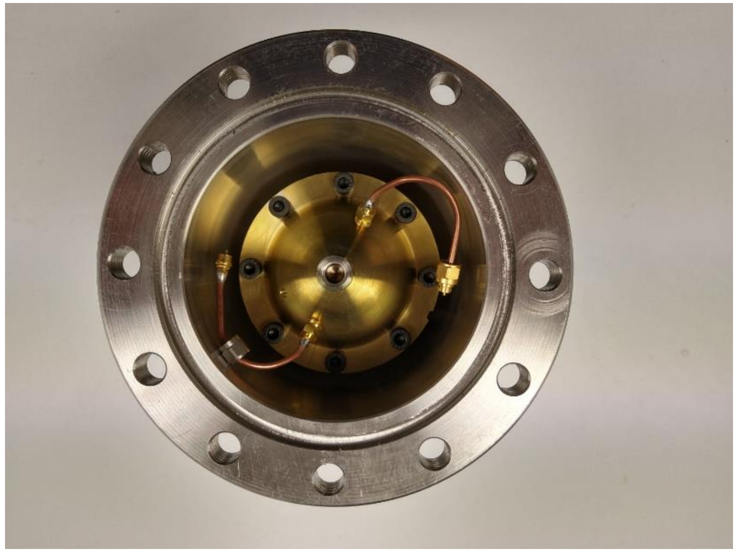
Activity 2.2.4
UVa

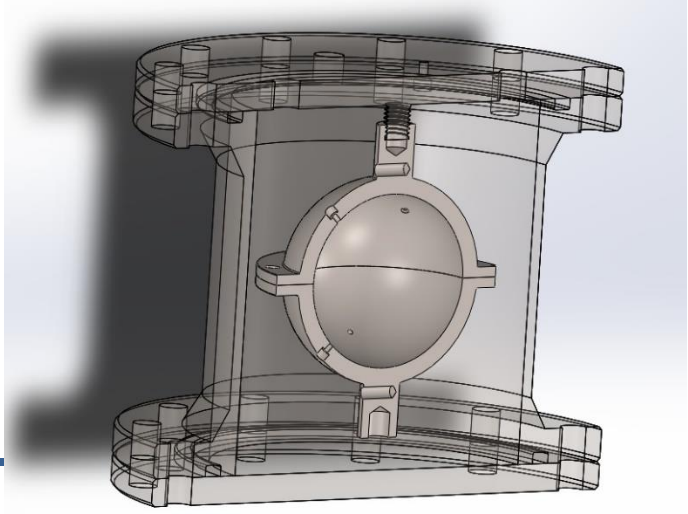
N_2, Ar, H_2 Impurities (H_2O): Accurate Thermophysics. *f*

Quasi-Spherical MW Resonator

200 K < T < 400 K $U(T)$ = 4 mK
p < 3 MPa $U_r(p)$ = 0.015%

D_x = 50.08 mm
D_y = 50.16 mm
D_z = 50 mm





- UVa designed and ordered the construction of a 4 cm diameter golden-plated quasi-spherical microwave resonator (QSMWR), 15 µm gold thickness. The new hygrometer is held in TermoCal UVa´s premises.
- The new QSMWR has been tested. Antennas have been tuned offering high quality resonant modes. Software has been upgraded and fully setup.

Activity 2.2.4
UVa

THUNDER SCIENTIFIC 4500

Dew point hygrometer, MBW, DP 30 model

New bath

- The construction of a new thermostat for the new QSMWR is completed.
- INTA has recalibrated the temperature and pressure sensors of the frost-point two pressure-two temperature saturation-based generator, an upgraded THUNDER SCIENTIFIC 4500 model, this equipment is now in TermoCal. INTA has calibrated of the transfer standard dew point hygrometer, MBW, DP 30 model, this equipment is now in TermoCal.
- The integration of the hygrometer, thermostat, QSMWR, control and software is being undertaken.

- **Task 2.2: Measurement of the enhancement factor in selected humid gas mixtures**

A2.2.4 M24	UVa will upgrade its microwave-based FP hygrometer to perform measurements of the enhancement factor of water vapour in N_2, Ar and H_2 in the FP range between (-75 and -30)°C at pressures from (0.1 to above 1) MPa. The traceability to FP temperature will be provided by INTA.	UVa, INTA

MILESTONES: ✓ Humidity Generator Portable + Chilled Mirror Hygrometer in UVa facilities

Assembled together with MW-based hygrometer → **FP temp. ≥ -30 °C**

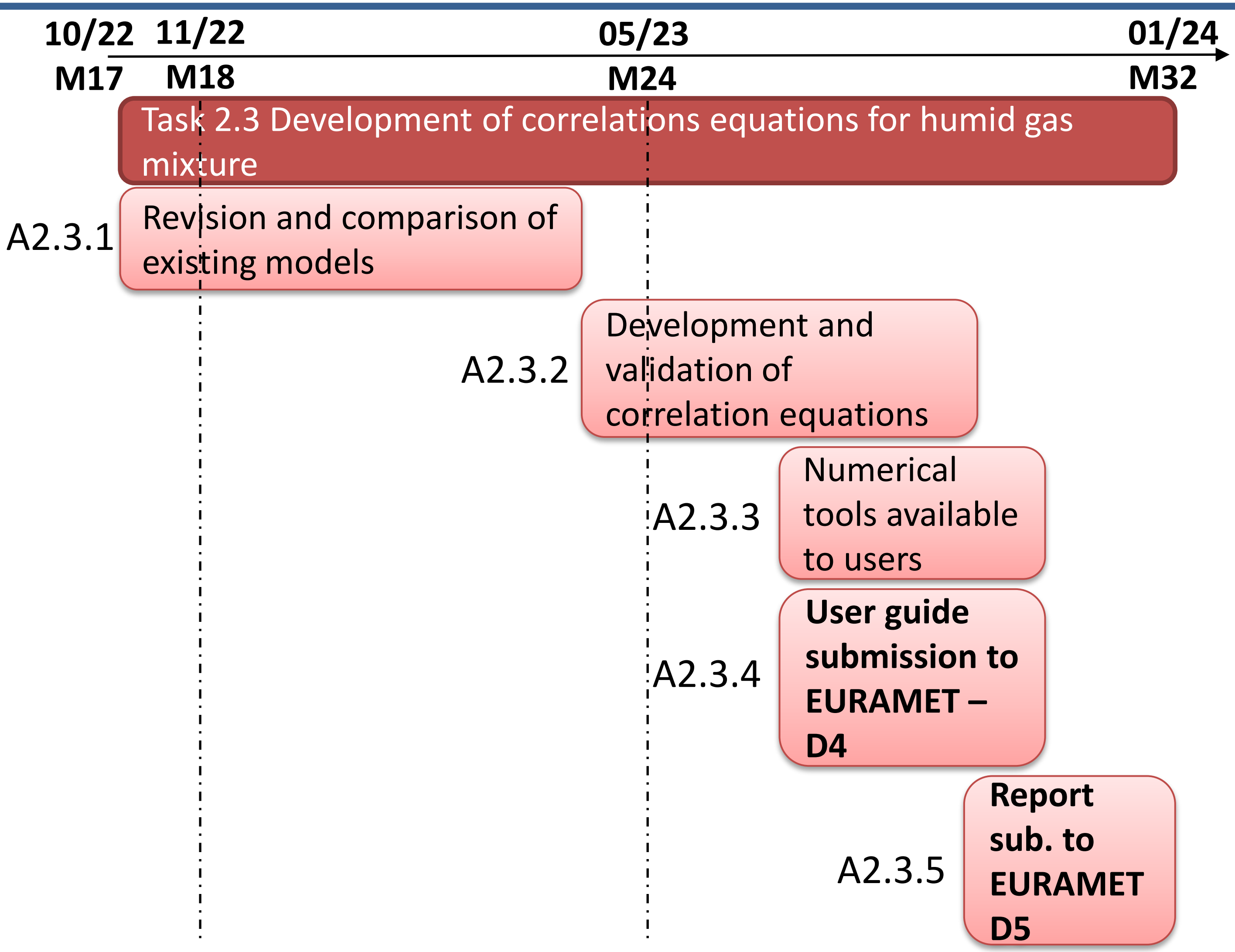
FUTURE ACTIONS: ❑ **Next Range Humidity Generator Portable + Chilled Mirror Hygrometer will be available.**

FP temp. ≥ -75 °C at 0.1 MPa in December.

ACTUAL STATUS: Supporting UVa needs
Delayed but under way

Task 2.3
Development of correlation equations for humid gas mixtures between -30 °C and -90 °C from 0.1 MPa to above 1 MPa

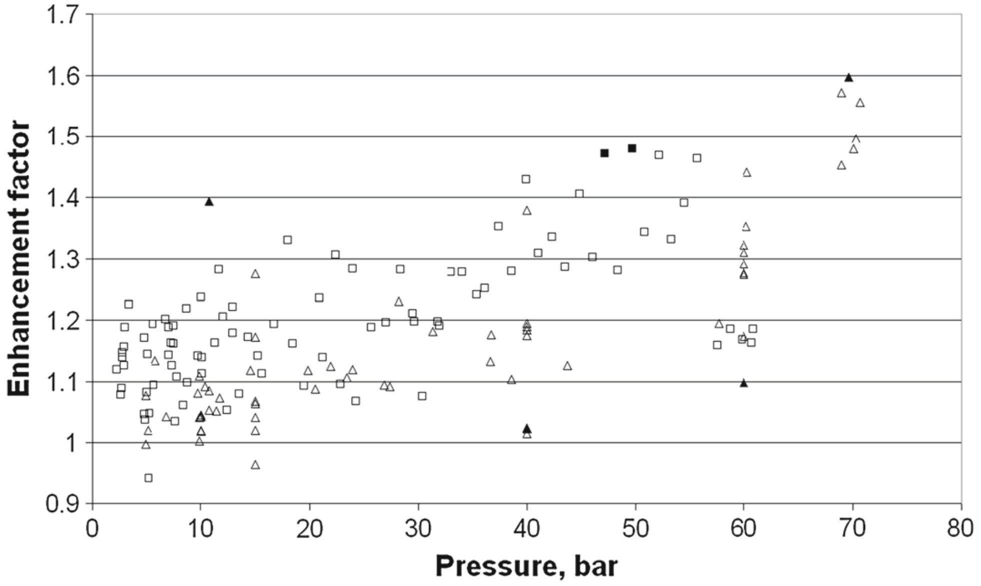
Task 2.3: Activities



Existing non-ideal humid gas mixtures models - UNICAS

UNIVERSITÀ DEGLI STUDI DI CASSINO E DEL LAZIO MERIDIONALE

Activity (Deadline)	Activity description	Partners
A2.3.1 (M23)	Activity started on M17 (October 2022). Collection of information from reports and published scientific papers related to non–ideal humid gas mixtures models. Moreover, UNICAS will review and compare the existing non–ideal humid gas mixtures models, with particular emphasis for nitrogen, argon and hydrogen.	**UNICAS**



Enhancement Factor for Water Vapor – Pressure Correction in Humid Methane

H. A. Sairanen, M.O. Heinonen

H
Hydrogen
Atomic Number: 1
Protons: 1
Atomic Mass: 1.0079

Ar
Argon
Atomic Number: 18
Protons: 19
Atomic Mass: 39.948

N
Nitrogen
Atomic Number: 7
Protons: 7
Atomic Mass: 14.0067

Int J Thermophys (2014) 35:1280–1289 1285

Table 2 List of previous methane water content studies with their publication year and pressure and temperature ranges

Reference	Year of publication	Temperature range (K)	Pressure range (MPa)
Chapoy et al. [6]	2005	277.8–297.9	0.491–4.374
Chapoy et al. [7]	2005	283.08–318.12	1.006–34.610
Folas et al. [5]	2007	253.15–293.15	1.5–18.0
Mohammadi et al. [3]	2004	282.98–313.12	0.510–2.846
Reshadi et al. [4]	2011	283.15–293.15	1–10
Sloan et al. [8]	1976	249.96–280.02	6.902–7.067

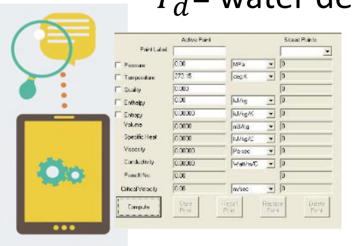
Activity 2.3.1

Numerical simulation of the correlation equations - UNICAS

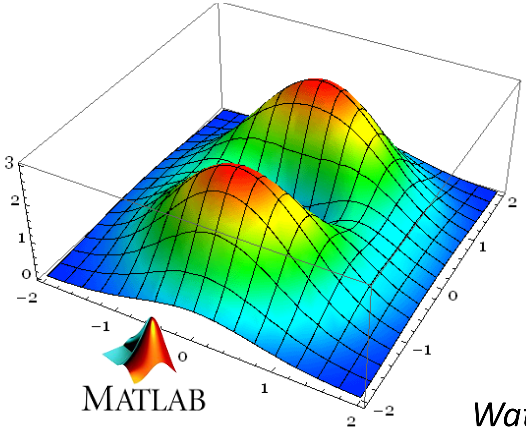
Activity (Deadline)	Activity description	Partners
A2.3.3 (M30)	Activity will start on M27. Based on the report regarding the improved measurements for water vapour enhancement factors from A2.2.5, UNICAS and VTT will implement and validate numerical tool(s), such as LabView, Matlab script, Java, Visual basic script or the like, to estimate the enhancement factor and its uncertainty in nitrogen, argon and hydrogen in the temperature range between -90 °C and -30 °C at selected pressures from 0.1 MPa to above 1 MPa. The validated numerical tool(s) will be software-implemented and be made freely available to the users in the form of a web-based application.	**UNICAS**, VTT

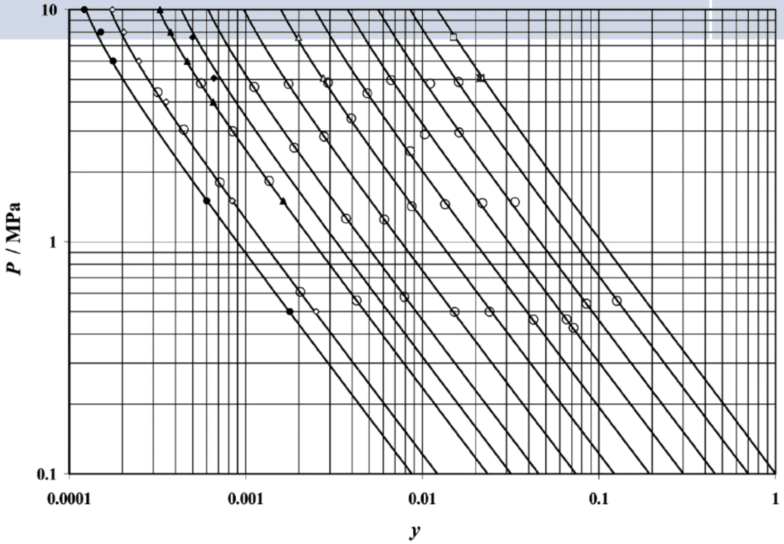
$$f(p, T_d) = \frac{y\,p}{e_w}$$

f = water vapour enhancement factor
y = amount fraction of water vapour
p = pressure of the gas mixture
e_w = water vapour pressure
T_d = water dew-point temperature



web-based application





Water content (mole fraction), y, in the vapour phase of the nitrogen obtained for a temperature between 278.15 K and 373.15K

PROMETH2O

Thank you for your attention

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