PROMETH2O

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WP2
Provision of robust traceability to trace water measurements in real humid gas mixtures

Lead INRIM

14th of June 2021

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

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Active partners in WP2

WP1 Methods

WP4 Impact

WP2 Traceability

WP5 Management

WP3 Demonstration

INRiM ISTITUTO NAZIONALE DI RICERCA METROLOGICA

PTB Physikalisch-Technische Bundesanstalt Braunschweig und Berlin

CEM CENTRO ESPAÑOL DE METROLOGÍA

Univerza v Ljubljani

CETIAT ensemble, innover et valider

UNIVERSITÀ DEGLI STUDI DI CASSINO E DEL LAZIO MERIDIONALE

ČESKÝ METROLOGICKÝ INSTITUT

UVa

le cnam

INSTITUTO NACIONAL DE TÉCNICA AEROESPACIAL

VSL

MBW calibration

VTT MIKES METROLOGIA

Objectives of the project in WP2

The specific objectives of this project are:

- 1. To improve trace water measurement methods in the amount fraction range between 5 parts in 10^6 (5 ppm) and 5 parts in 10^9 (5 ppb) or, equivalently, between -65 °C and -105 °C frost point temperature at 0.1 MPa with a relative standard uncertainty between 3 % and 8 %, from the upper to lower range, respectively.

WP2

- **2. To provide robust traceability to trace water measurements by developing suitable primary standards for the amount fraction range from 5 ppm to 5 ppb (or -65 °C to -105 °C frost point temperature at 0.1 MPa) with a relative standard uncertainty less than 3 % to 8 %, in selected gas matrices of air, N_2, Ar and H_2 at pressures up to 1 MPa.**
- **3. To improve the present knowledge of thermophysical data of real humid gas mixtures, in particular the water vapour enhancement in N_2 and Ar in the temperature range from -30 °C to -90 °C and at pressures from 0.1 MPa to above 1 MPa.**
- 4. To demonstrate improved trace water measurement methods between 5 ppm and 5 ppb or, equivalently, between -65 °C and -105 °C frost point temperature at 0.1 MPa, in two industrially relevant facilities (test beds).
- 5. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain, standards developing organisations (CIPM, IAPWS, JCS) and end users (instrument manufacturers, gas providers).

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WP2 - Deliverables

Month	1	2	3	4
Activities	Jun-21	Jul-21	Aug-21	Sep-21
	WP2			
	Task 2.1			
A2.1.1				
A2.1.2				
A2.1.3				
A2.1.4				
A2.1.5				
A2.1.6				

2 (A2.1.7)	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	Report	**INRIM**, VTT, CMI, INTA, UL, PTB, MBW, VSL, CETIAT	Nov 2023 (M30)

D3

3 (A2.3.4)	D4	User guide related with the software tool(s) of a web-based application to estimate the enhancement factor and uncertainty in water vapour in N_2, Ar and H_2 in the temperature range between -30 °C and -90 °C and	User guide	**UNICAS**, VTT	Nov 2023 (M30)

3 (A2.3.5)	D5	Report on the development and validation of correlation equations for the enhancement of water vapour in N_2, Ar and H_2 in the temperature range from -30 °C to -90 °C and at pressures from 0.1 MPa to above 1 MPa	Report	**VTT**, CNAM, CETIAT, CMI, VSL, UL, INTA, CEM, UVa, UNICAS	Jan 2024 (M32)

D4

D5

Work Package 2 Aim

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**)

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

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

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

To develop, extend or improve primary standards that in combination will generate reference humidity quantities, such as dew/frost-point temperature and amount fraction of water vapour, in the targeted range of pressure and temperature.

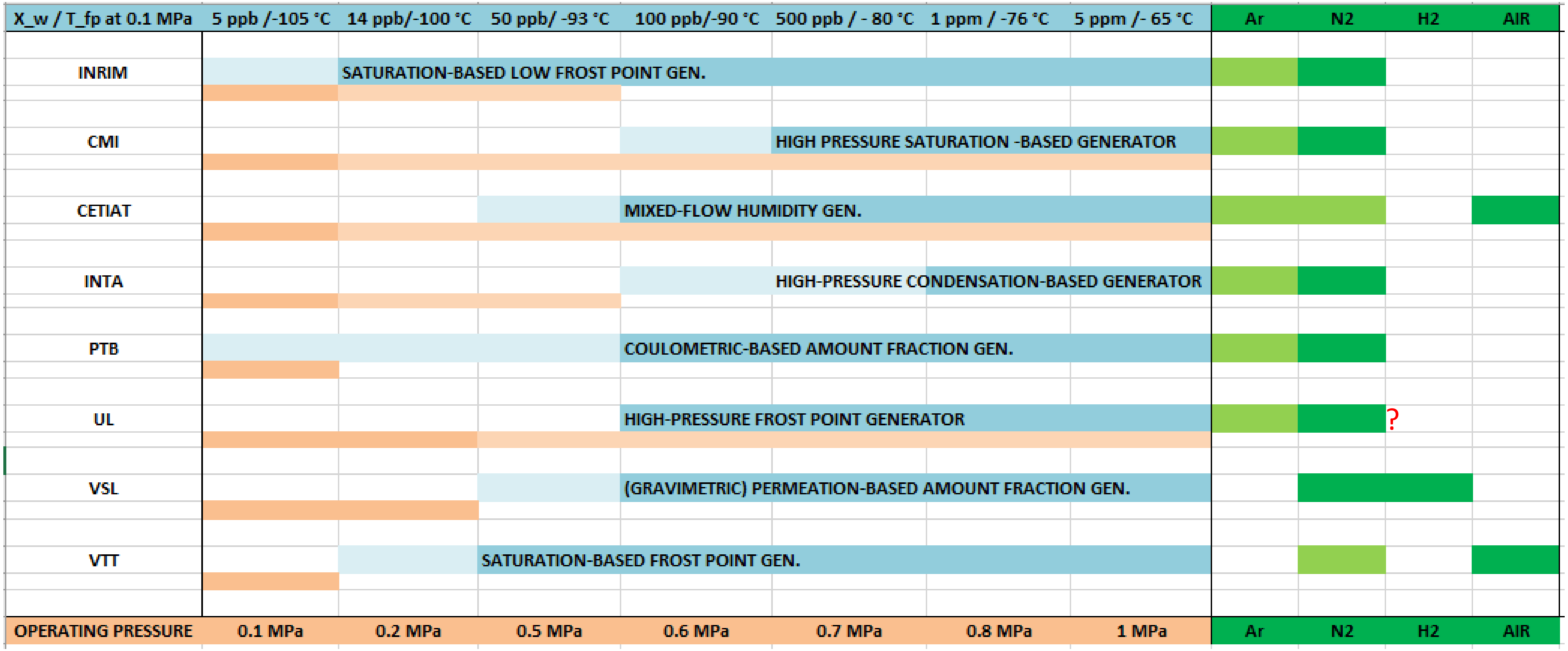
GOAL

The amount fraction range from 5 ppm to 5 ppb (or -65 °C to -105 °C frost point temperature at 0.1 MPa) with a relative standard uncertainty less than 3 % to 8 %, in selected gas matrices of air, N_2, Ar and H_2 at pressures up to 1 MPa.

TECHNIQUES

- **Thermodynamic-based standard generators with the ability to generate frost-point temperatures between -65 °C and -105 °C with a target uncertainty of 0.35 °C at the lowest temperature.**
- **Water vapour amount fraction generators aimed to cover the range between 5 $\mu mol \cdot mol^{-1}$ (5 ppm) and 5 $nmol \cdot mol^{-1}$ (5 ppb) with a standard relative uncertainty of 3 % to 8 %, respectively.**

Task 2.1 – Present and improved capabilities



Task 2.1 - Activities

Activity number	Activity description	Partners
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
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
A2.1.3 M30	**PTB, with instrument support from MBW**, will extend the lower limit of a coulometric-based primary standard generator to generate **down to 5 ppb** reference amount fractions of water vapour in **nitrogen at 0.11 MPa** and will develop the primary humidity standard **for use with argon**. The development of such a standard by PTB will extend the reference values with **relative standard uncertainties of 8 % at the lower limit**, not including the "zero gas" uncertainty, which is conservatively estimated to be ±3 ppb. PTB will use the standard to test selected instruments for amount fraction water vapour measurement, such as CC-FS-CRDS spectrometer (A1.1.1), high-quality CMH, CE-FM spectroscopy hygrometer (A1.1.4), or far-UV system (A1.1.2). PTB will take the decision about which hygrometers will be used for the test at a later stage.	**PTB**, MBW

Task 2.1 - Activities

Activity number	Activity description	Partners
A2.1.4 M21	**VSL** will set up a permeation system based on a passivated magnetic suspension balance to generate primary standard of water amount fractions in **nitrogen** and **hydrogen** in the range of **50 nmol/mol up to 5 µmol/mol** following ISO 6145-10 and ISO 6145-7.	**VSL**
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**
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
A2.1.7 M30 D3	**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

INRIM development in WP2-Task 2.1

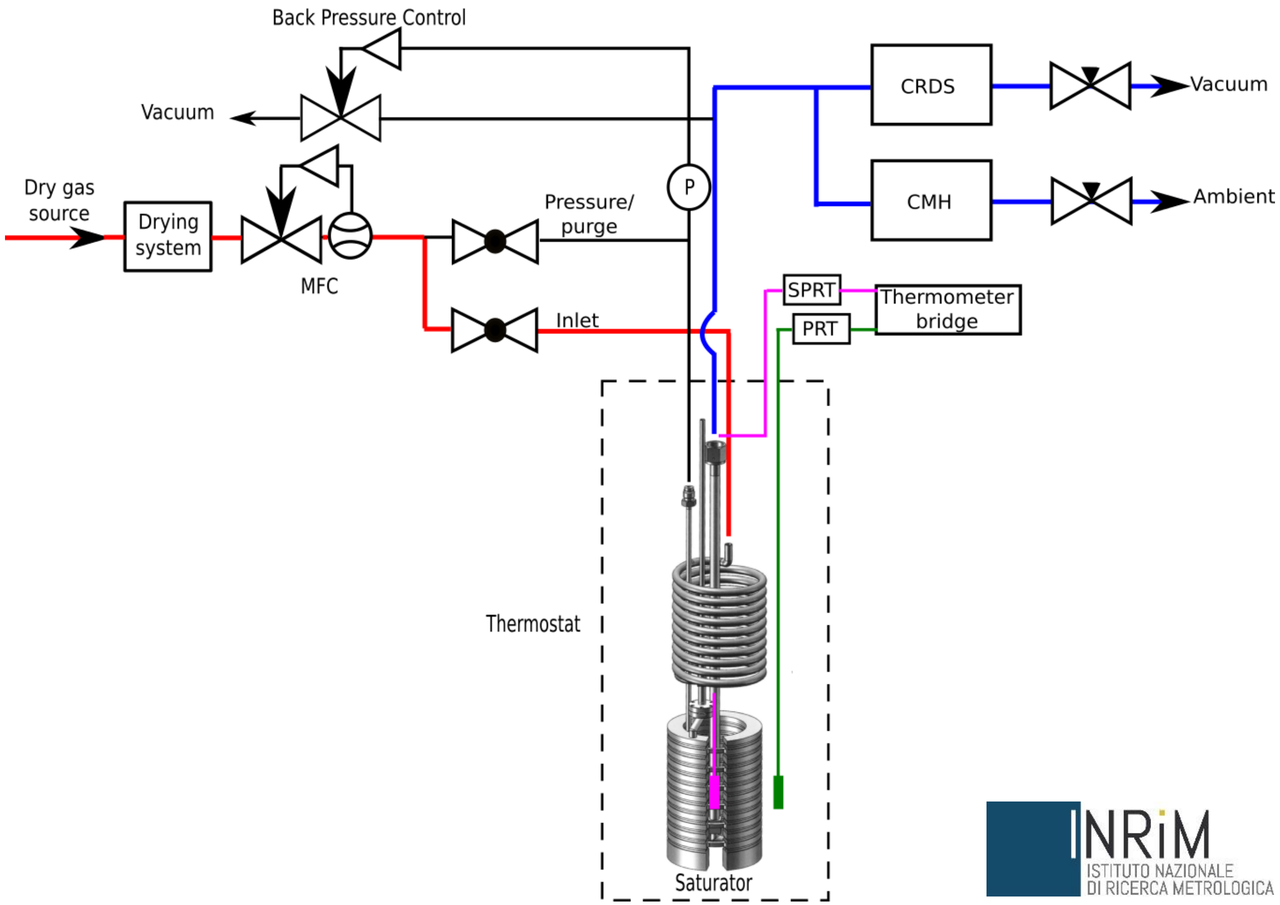
❑ **A2.1.1 (M21)**: Improvement of its thermodynamic saturation-based primary standard generator.

- **Frost point temperature: -99 °C to -20 °C**
- *U*(*T*=-95 °C) = 0.05 °C
- *P*: 200 hPa to 1100 hPa
- x_w: 15 nmol/mol to 0.005 mol/mol
- Nitrogen

PRESENT CAPABILITY

- **Frost point temperature: -105 °C to -20 °C**
- *U*(*T*=-105 °C) = 0.35 °C
- *P*: 200 hPa to 5000 hPa
- x_w: 5 nmol/mol to 0.005 mol/mol
- Nitrogen, argon, (air)

FEBRUARY 2023



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PTB contribution to WP2-Task 2.1

- **Activity 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)

- **Activity 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)

- **Activity 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)

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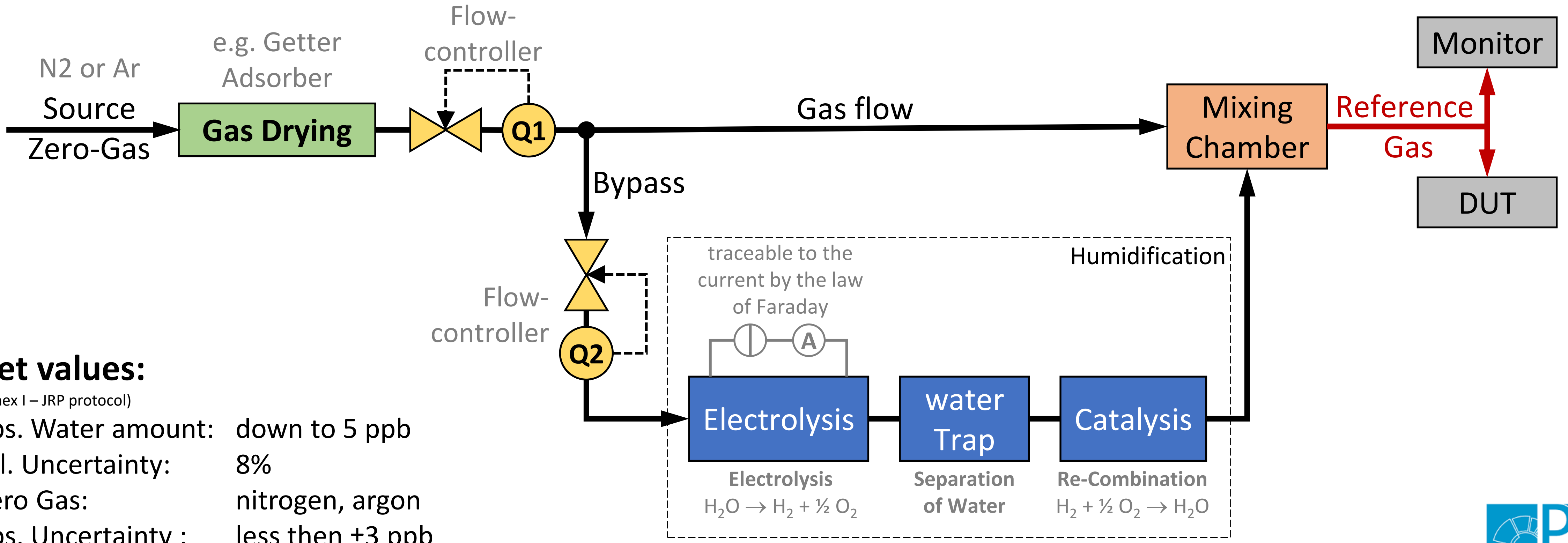
Activity 2.1.3 (PTB Development)

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

Survey of current and next steps (PTB)

Steps already in progress

- Recruiting of additional personal
- Development of a concept (Basic setup)
- Preliminary tests (Zero-Gas Quality)

Schedule for major steps

• Elaboration of design	21/22
• Acquisition of hardware	end 21/22
• Construction of the apparatus	22/23
• Commissioning and measurements	23

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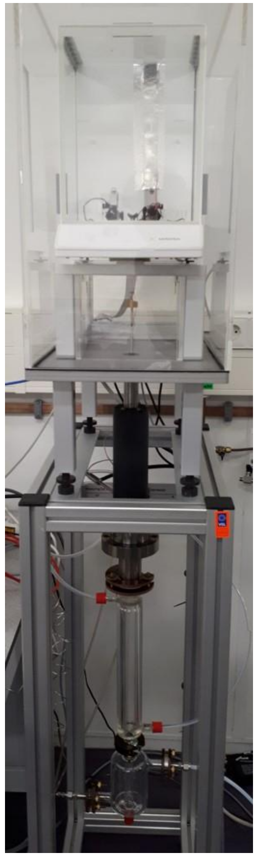
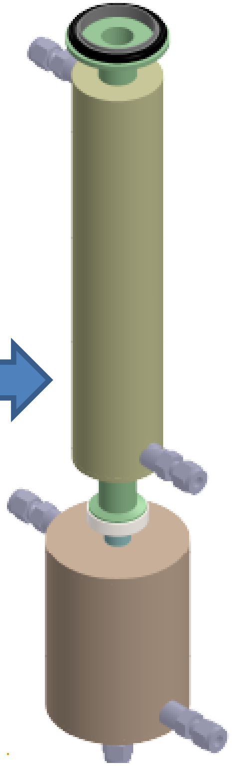
VSL contribution to WP2-Task 2.1

- **A2.1.4 (M21)**: Permeation system based on a passivated magnetic suspension balance.



now



later

- 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 to take:

1) **Complete design and manufacturing metal chamber with reduced nr of connections**
2) **Install new permeation chamber and surrounding dry zone**
3) **Testing and validation of the new system**

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

To evaluate the non-ideality of gas mixtures with trace amount of water.

GOAL

Improving of the data available for water vapour enhancement factor in air, N_2, Ar and H_2 in the frost-point temperature range between -90 °C and -30 °C and pressures from 0.1 MPa to above 1 MPa.

METHOD

A series of cross domain experiments that rely on trace humidity standards developed in Task 2.1 and amount-of-substance measurements methods made available in WP1.

Task 2.2 - Activities

	AMOUNT FRACTION AND EQUIV. FROST POINT TEMPERATURE						MATRIX GAS		
X_w / T_fp at 0.1 MPa	100 ppb/-90 °C	500 ppb / - 80 °C	1 ppm / -76 °C	5 ppm / - 65 °C	83 ppm / -40 °C	382 ppm/ -30 °C	Ar	N2	H2
CEM				GAS MIXTURES IN CYLINDERS					
CMI		HIGH-PRESSURE SATURATION-BASED GENERATOR							
CETIAT, CNAM				MICROWAVE-BASED TRACE WATER ANALYSER					
INTA			HIGH-PRESSURE CONDENSATION-BASED GENERATOR						
VSL		HIGH-PRESSURE FROST POINT GENERATOR							
UL		HIGH-PRESSURE FROST POINT GENERATOR							
UVa				MICROWAVE-BASED FROST POINT HYGROMETER					
OPERATING PRESSURE	0.1 MPa	0.2 MPa	0.5 MPa	0.7 MPa	0.8 MPa	1 MPa	Ar	N2	H2

Task 2.2 - Activities

Activity number	Activity description	Partners
A2.2.1 M24	**CNAM and CETIAT** using the facility developed in A2.1.5, will upgrade CNAM microwave-based trace water analyser to perform measurements of the enhancement of water vapour in **nitrogen** and **argon** in the frost-point temperature range between **-80 °C and -30 °C** at selected pressures **from 0.1 MPa to above 1 MPa**.	**CNAM**, CETIAT
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
A2.2.3 M18	**CEM**, will produce cylinders containing static, pressurised humid gas reference 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 by UVa and will further develop and upgrade its microwave-based frost point hygrometer.	**CEM**, UVa

Task 2.2 - Activities

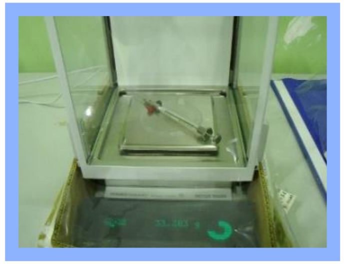
Activity number	Activity description	Partners
A2.2.4 M24	**UVa and INTA**, using the upgraded saturation-based generator from A2.1.2 and upgraded microwave-based frost point hygrometer in A2.2.3, will perform measurements of the enhancement of water vapour in **nitrogen, argon and hydrogen** in the frost-point 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.	**UVa**, INTA
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

CEM contribution to WP2-Task 2.2

- **A2.2.3 (M18)**: Production of cylinders containing humid gas reference mixtures in matrices of N_2, Ar and H_2 with x_w down to 1 µmol mol^{-1}.

I)

ISO 6142-1:2015
Gas analysis -- Preparation of calibration gas mixtures -- Part 1: Gravimetric method for Class I mixtures



II)

N_2 / H_2 / Ar

H_2O < 1 ppm

CRDS

UVa Universidad de Valladolid

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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

GOAL

- To improve the humid gas mixtures correlation equations in the temperature range between -30 °C and -90 °C at pressures from 0.1 MPa to above 1 MPa for N_2, Ar and H_2.
- To offer a tool to end users for a better comparability of trace humidity measurements based on different principles and gas matrices.

METHOD

Modelling, simulation and validation of the correlation equations for the water vapour enhancement factor starting from existing non-ideal humid gas mixtures models.

Task 2.3 - Activities

		AMOUNT FRACTION AND EQUIV. FROST POINT TEMPERATURE					MATRIX GAS		
X_w / T_fp at 0.1 MPa	100 ppb/-90 °C	500 ppb / - 80 °C	1 ppm / -76 °C	5 ppm / - 65 °C	83 ppm / -40 °C	382 ppm/ -30 °C	Ar	N2	H2
VTT		MODELLING AND CORRELATION EQUATIONS							
UNICAS			MODELLING AND SIMULATION						
OPERATING PRESSURE	0.1 MPa	0.2 MPa	0.5 MPa	0.7 MPa	0.8 MPa	1 MPa	Ar	N2	H2

Task 2.3 - Activities

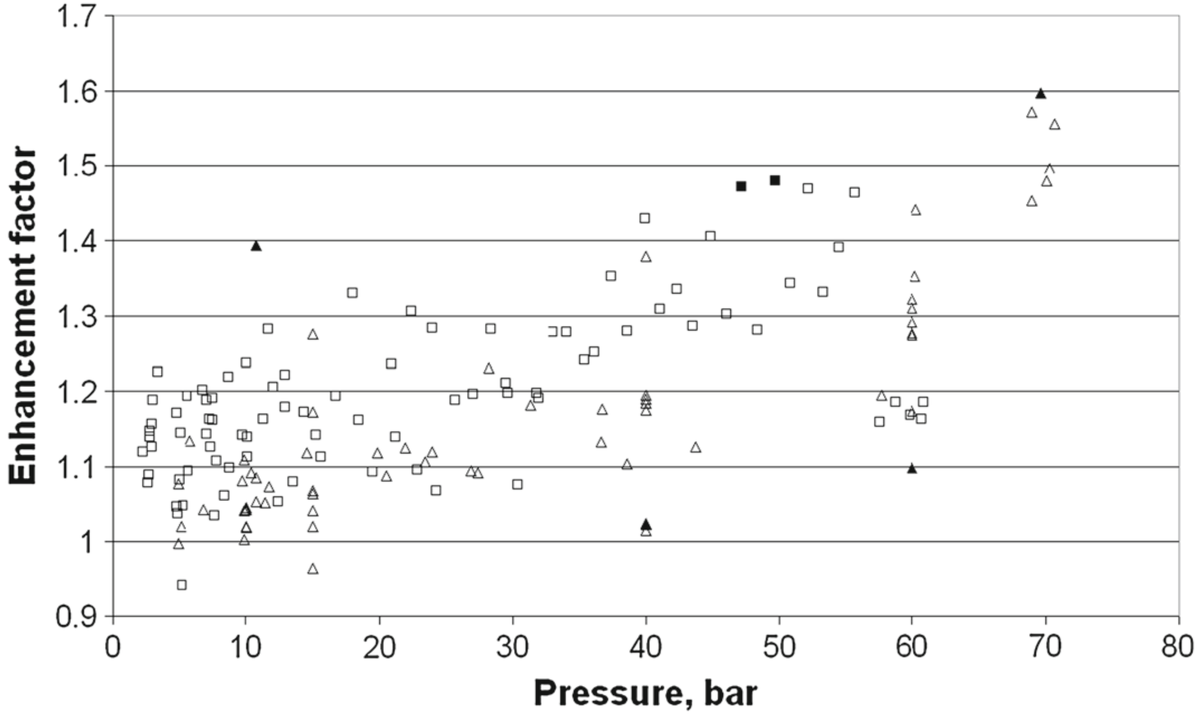
Activity number	Activity description	Partners
A2.3.1 M23	**UNICAS** will **collect information** from reports and published scientific papers related to non–ideal humid gas mixtures models. Moreover, UNICAS will **review and compare** the **existing non–ideal humid gas mixtures models**, with particular emphasis for nitrogen, argon and hydrogen.	**UNICAS**
A2.3.2 M29	**VTT, and UNICAS**, using the report on the improved measurements for water vapour enhancement factors from A2.2.5 and the reviewed information from A2.3.1, will **develop and validate** the correlation equations for the enhancement of water vapour in **nitrogen, argon and hydrogen** in the temperature range between **-90 °C and -30 °C** and pressure range from **0.1 MPa to** above **1 MPa** .	**VTT,** UNICAS
A2.3.3 M30	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

Task 2.3 - Activities

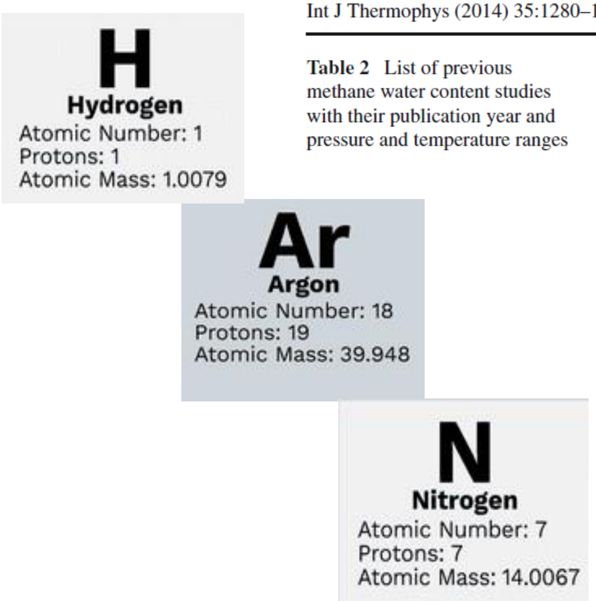
Activity number	Activity description	Partners
A2.3.4 M30 D4	**UNICAS and VTT** will write **a report** using the data from A2.2.5 and A2.3.3. Once the report has been agreed by the consortium, the coordinator on behalf of UNICAS, and VTT, will then submit it to EURAMET as **D4: *'User guide related with the software tool(s) of a web-based application to estimate the enhancement factor and uncertainty in water vapour in N2, Ar and H2 in the temperature range between -30 °C and -90 °C and pressure range from 0.1 MPa to above 1 MPa***.'	**UNICAS,** VTT
A2.3.5 M32 D5	**VTT** will write **a report** using the report from A2.2.5 and the developed equation in A2.3.2. VTT and UNICAS will review the report and will send it to the coordinator. Once the report has been agreed by the consortium, the coordinator on behalf of VTT and UNICAS, will submit it to EURAMET as **D5: *'Report on the development and validation of correlation equations for the enhancement of water vapour in N2, Ar and H2 in the temperature range from -30 °C to -90 °C and at pressures from 0.1 MPa to above 1 MPa.'***	**VTT,** UNICAS

UNICAS contribution to WP2-Task 2.3

- **A2.3.1 (M23)**: Revision and comparison of existing non-ideal humid gas mixtures models.



Enhancement Factor for Water Vapor – Pressure Correction in Humid Methane - H.A. Sairanen, M.O. Heinonen



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

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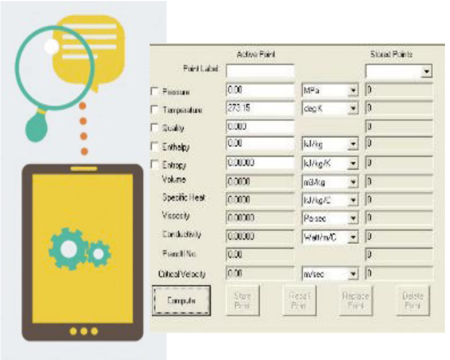
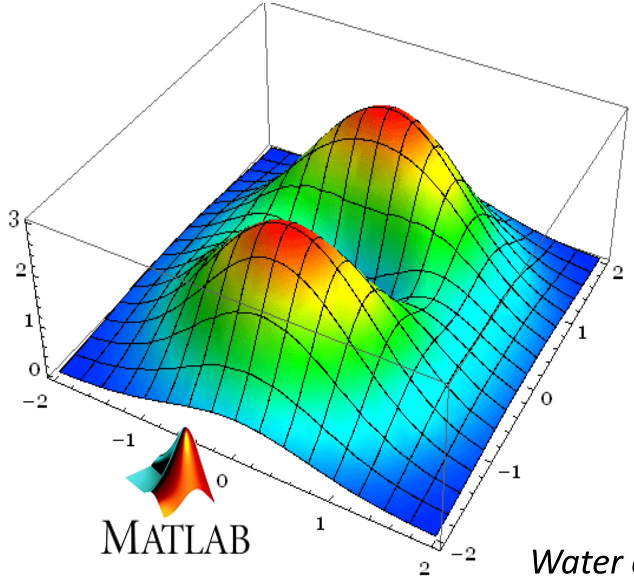
- **A2.3.3 (M30)**: Implementation and validation of **numerical simulation of the correlation equations**

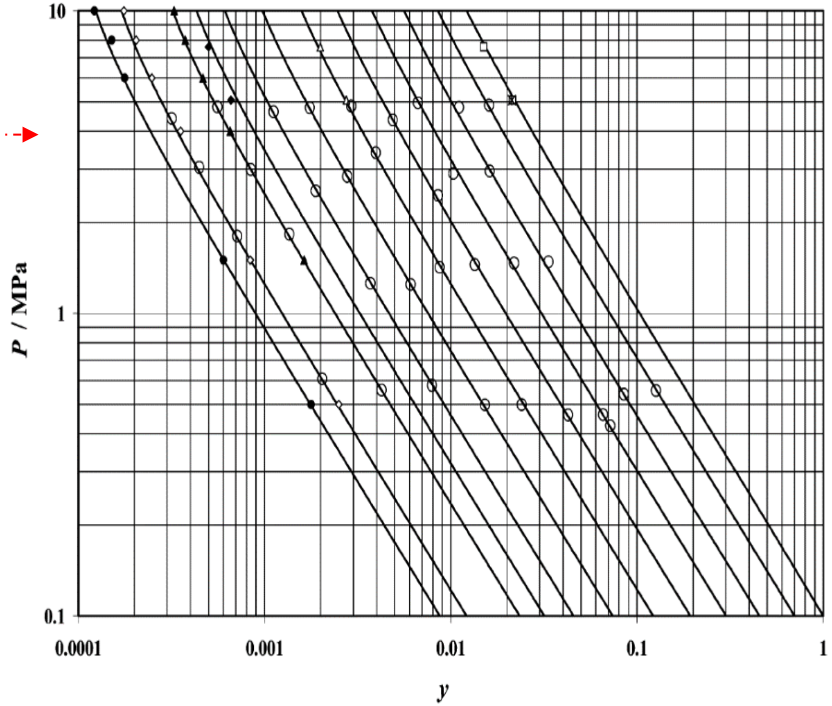
$$f(p, T_d) = \frac{y\,p}{e_w}$$

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

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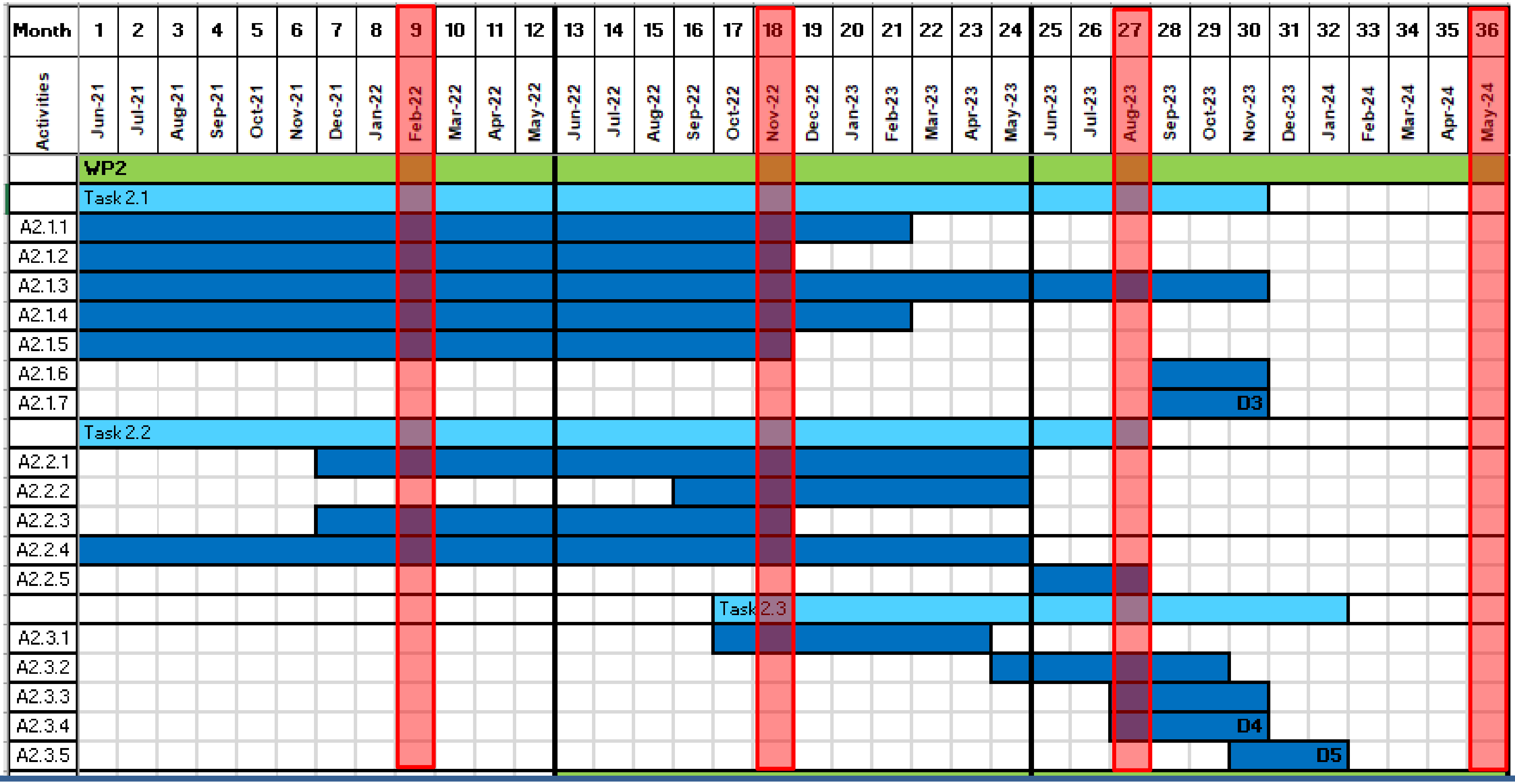
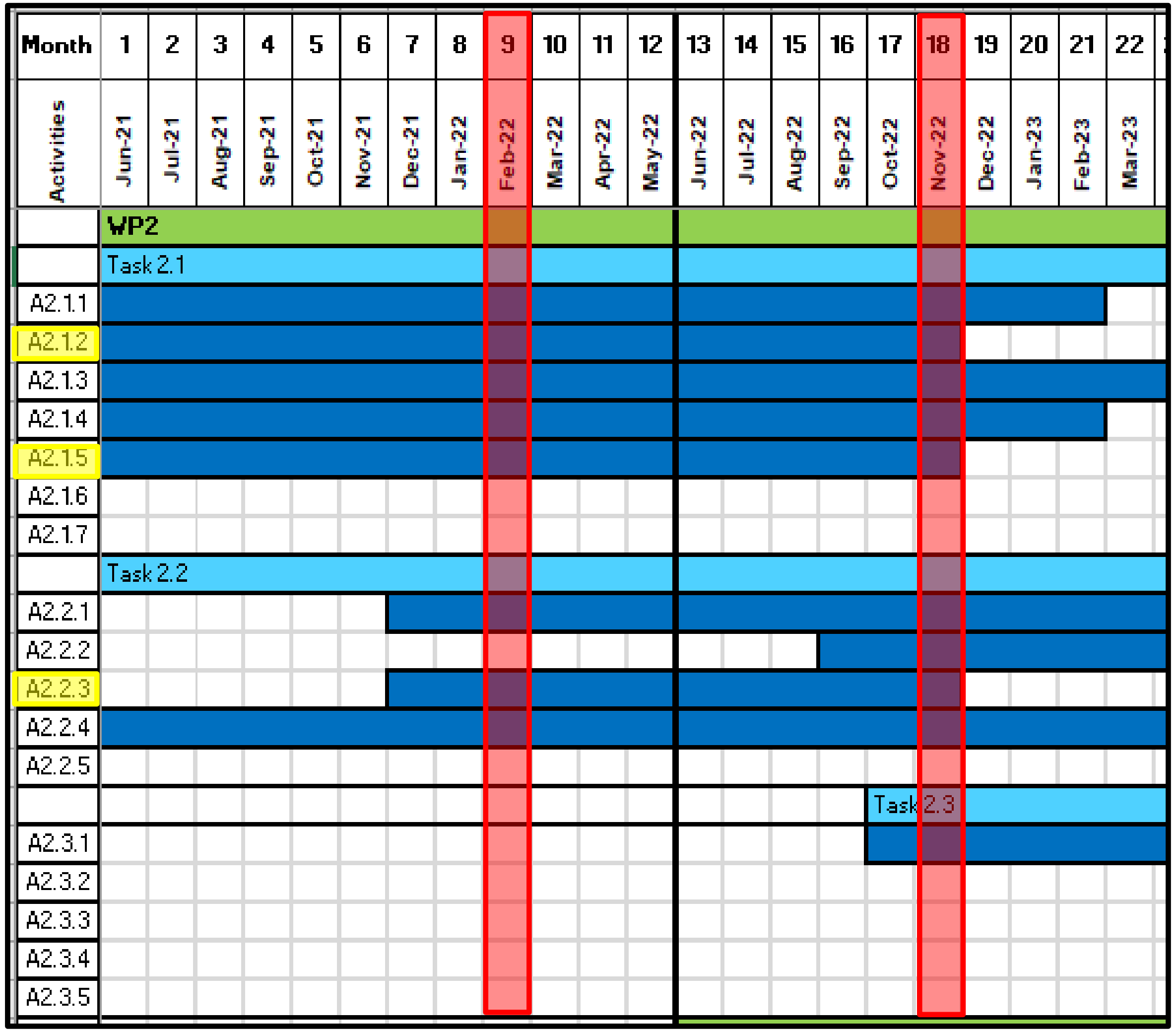
Milestones and reporting



Reporting period

1^{st} milestone Feb. 2022 (M9)

- **A2.1.2** CMI, INTA and UL will upgrade their saturation-based generators to produce humid gas mixtures in N_2 and Ar to extend the limit of reference frost-point temperatures to -90 °C and pressures up to 1 MPa.
  CMI, INTA, UL **- Report due Nov. 2022**
- **A2.1.5** CETIAT will upgrade its mixed flow generator in pressure, from 0.1 MPa up to 1 MPa, and in frost point temperature down to -90 °C (possibly -95 °C).
  CETIAT - Report due Nov. 2022
- **A2.2.3** CEM, will produce cylinders containing pressurised humid gas reference mixtures in matrices of N_2, Ar and H_2 with amount fractions of water vapour to 1 µmol mol^{-1}. UVa will further develop and upgrade its microwave-based frost point hygrometer.
  CEM, **UVa - Report due Nov. 2022**



Thank you for your attention

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