PROMETH$_2$O

20IND06 PROMETH2O

WP2

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

Project Meeting at M27

Online

21 September 2021

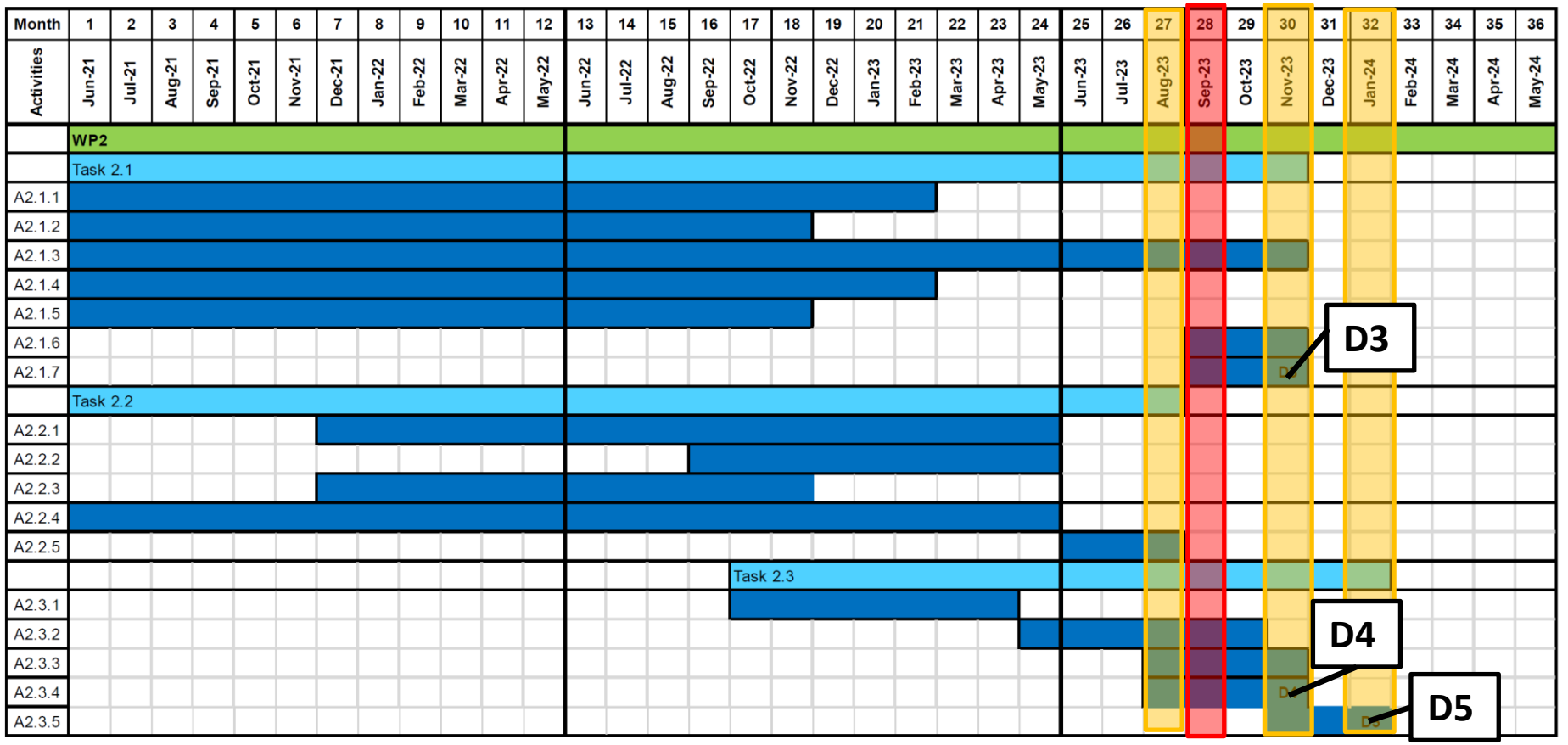
EMPIR EURAMET

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**)



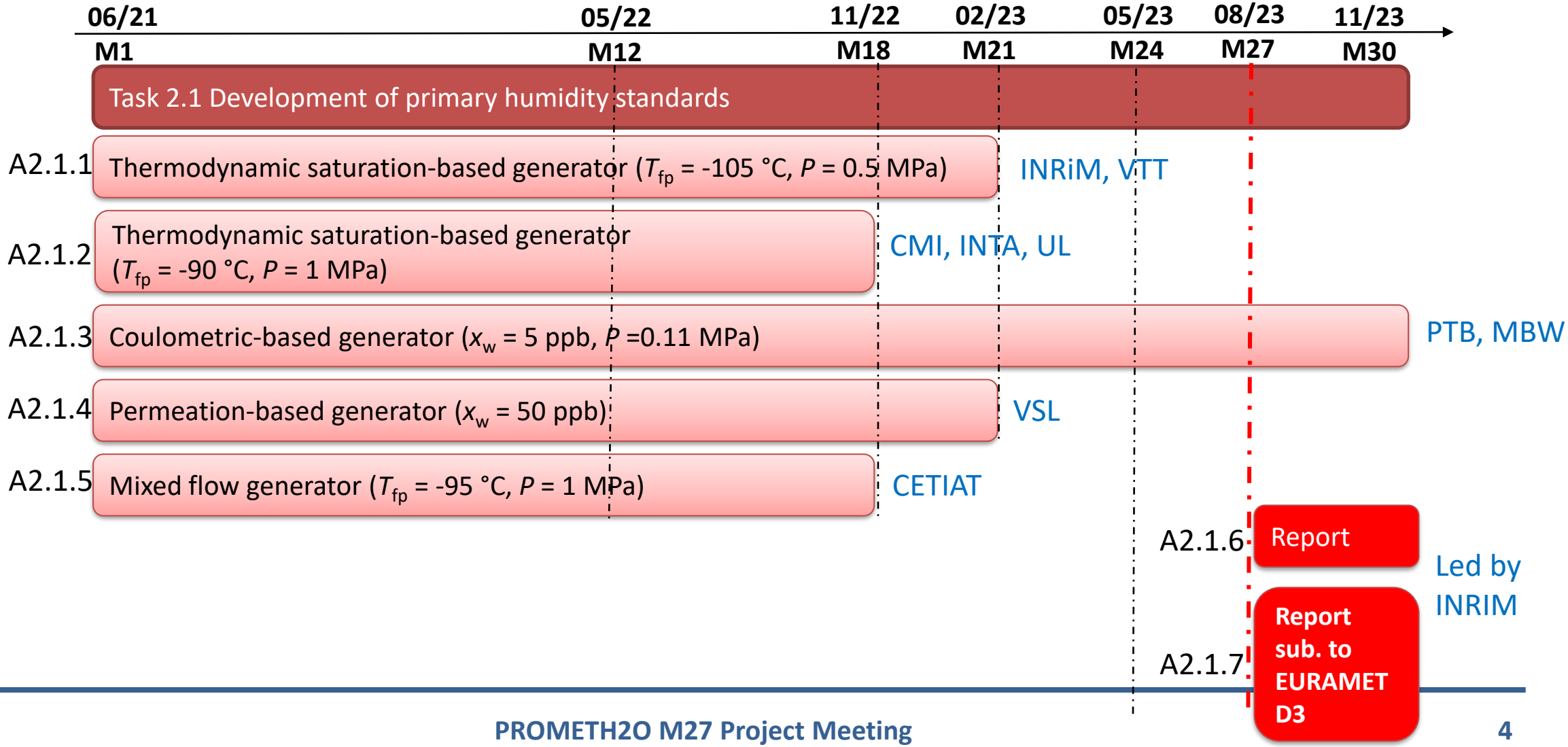
Last WP2 monthly meeting – 4 Sept 2023

Several delays due to:

- Experimental issues
- Lack of staff

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

Task 2.1: Activities



Activity 2.1.1
INRIM, VTT

Delay

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

INRIM: The definition of the uncertainty budget is underway.

VTT: The system is under characterisation. The plan is to finalise everything by October 2023.

Activity 2.1.2
CMI, INTA, UL

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

Delay

CMI: The traceability of all the equipment was checked. Argon measurements finalized at -80 °C and -70 °C at different pressures. Last measurements at -60 °C and data analysis underway .

INTA: The calibration of the new low frost point generator based on the critical flow nozzle is underway with all required fluids prepared; the existing generator is operational; the characterisation of the hygrometers for the new generator has begun. **(Extremely Delayed - maybe activity completed by M36).**

UL: Generator basically ready, however still waiting for the new LX to arrive by the end of the week.

Activity 2.1.3
PTB

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

Delay

PTB: From 2 to 4 weeks of delay. At the moment completion of the activity by M30 is more likely than M29.

Activity 2.1.4
VSL

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**

Delay

VSL: Technical issue to be solved by the manufacturer of the suspension balance. Then, collection of data. The expectation is for all experiments to be completed by October **(Delayed M29 – October 2023)**

Activity 2.1.5
CETIAT

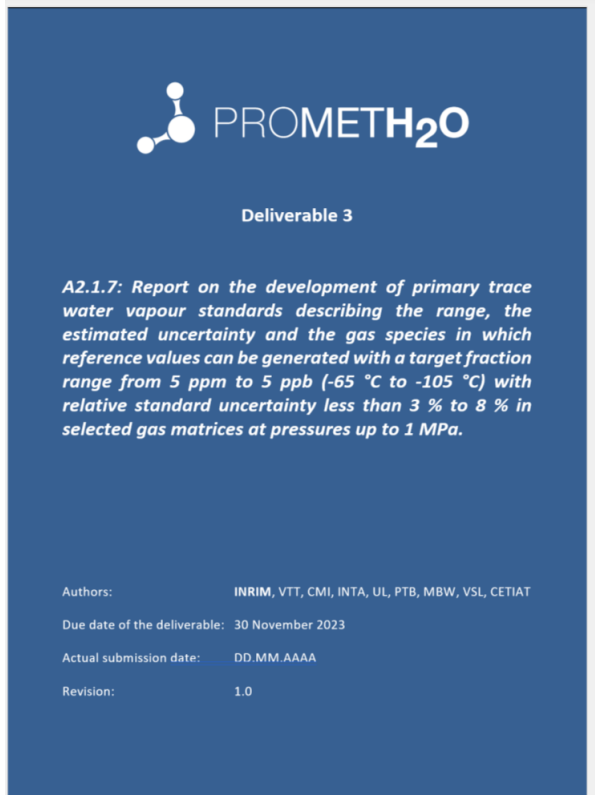
A2.1.5 M18	CETIAT will upgrade its mixed flow generator in pressure, from 0.1 MPa up to 1 MPa, and in frost point temperature, from -85 °C down to -90 °C, possibly -95 °C, with a standard uncertainty of 0.25°C.	**CETIAT**

Delay

CETIAT: Late in autumn validation of the generator below -80 °C (-85 °C) and up to 1 MPa using the Tiger Optics CRDS borrowed from Process Insights. **(Delayed M29 – October 2023).** At the moment, the generator is at LNE-CNAM for performing the measurement campaign.

Deliverable D3: M30 - NOVEMBER 2023

INRIM sent a table of content (9 July 2023)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Deliverable 3

A2.1.7: 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.

Authors: **INRIM**, VTT, CMI, INTA, UL, PTB, MBW, VSL, CETIAT

Due date of the deliverable: 30 November 2023

Actual submission date: DD.MM.AAAA

Revision: 1.0

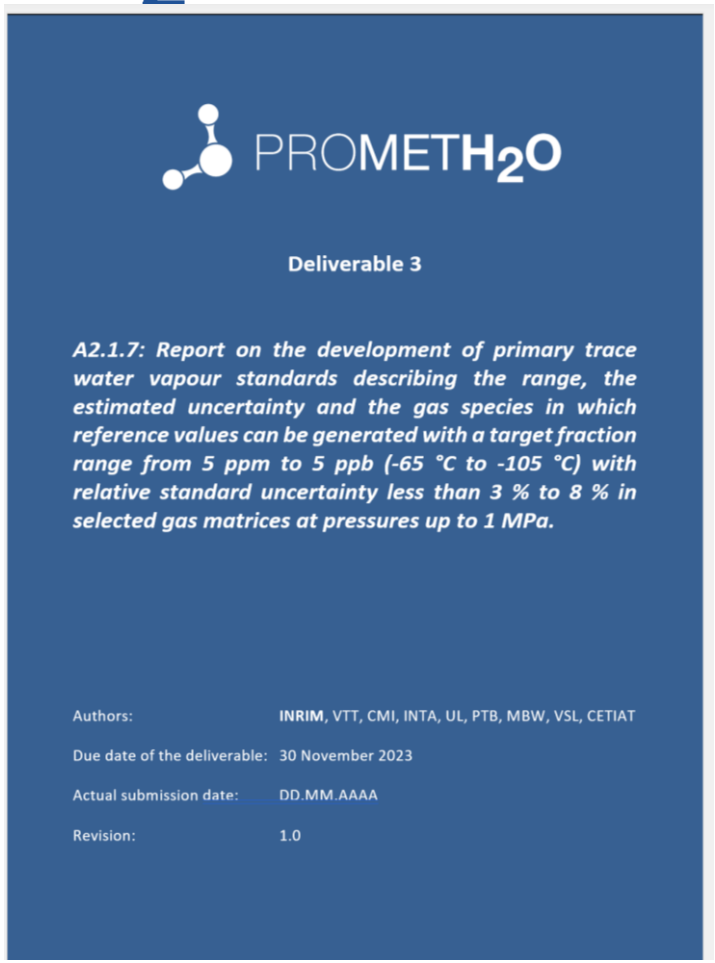
PROMETH2O A2.1.7 Deliverable3_v1.docx

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	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

All partners are asked to:

- **fill in the D3 fields they are responsible for by adding text and all information they already have about their standard generators;**
- **provide their contributions by 15 September 2023 (Friday), so that a first draft of the D3 deliverable can be discussed at the M27 meeting on 21 September.**

Deliverable D3: M30 - NOVEMBER 2023



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Deliverable 3

A2.1.7: 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.

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Due date of the deliverable: 30 November 2023

Actual submission date: DD.MM.AAAA

Revision: 1.0

PROMETH2O A2.1.7 Deliverable3_v1.docx

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.

Funding European Metrology Program for Innovation and Research	**Grant agreement n** 20IND06
Project name Metrology for trace water in ultra-pure process gases	**Project short name** PROMETH2O
Authors **Lead partner**: INRIM **Partners**: VTT, CMI, INTA, UL, PTB, MBW, VSL, CETIAT	**Pages** xx pages
Due date of the deliverable: 30 November 2023 **Actual submission date of the deliverable:** DD.MM.AAAA	**Revision** 1.0

Summary

This report was written as part of the activity A2.1.7 from the EMPIR 20IND06 PROMETH2O "Metrology for trace water in ultra-pure process gases" project.
The objective of the three-year EU project commenced on 1st June 2021 is to fill the knowledge gap regarding the metrological traceability by developing traceable and improved methods for trace water measurement to be used in the production and use of pure process gases at challenging amount fractions between 5 ppm and 5 ppb, and to demonstrate the relevant metrology practices in the industry supply chain.
For more details about this project please visit www.prometh2o.eu

This project (EMPIR 20IND06 PROMETH2O) has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme under Grant agreement No. 20IND06.

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

FIRST DRAFT

Contribution received from:

PTB
UL
VSL

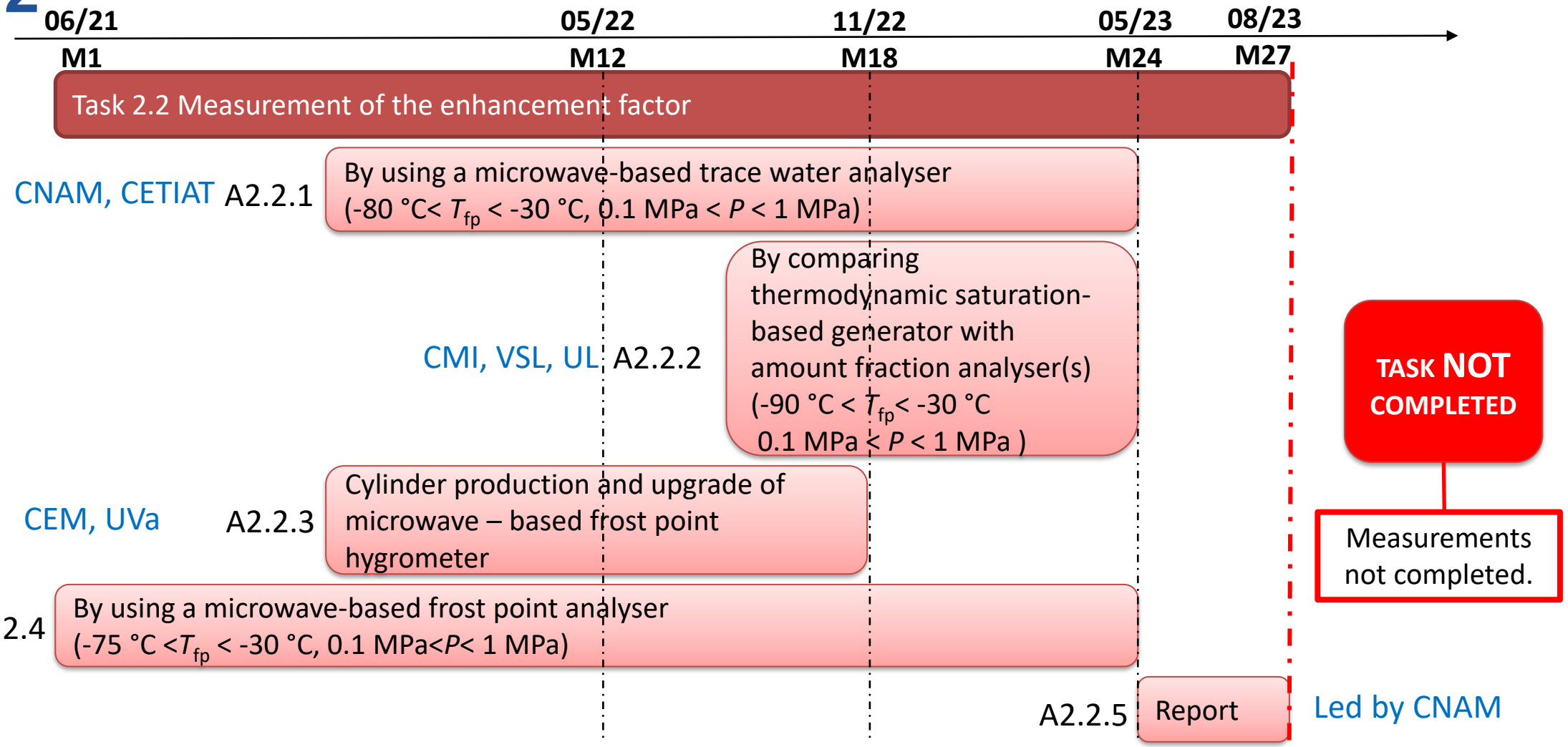
Missing:

CMI
VTT
INTA
INRIM
CETIAT

Ask to MSU to postpone the delivery date of D3

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

Task 2.2: Activities



Activity 2.2.1
CETIAT, CNAM

Activity number	Activity description	Partners (Lead in bold)
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

Delay

CETIAT: Generator moved to CNAM.

CNAM: Measurements of enhancement factor in Ar in the temperature range from -70 °C to -20 °C between 114 kPa and 186 kPa. Absolute measurement of *f*. Measurements to be started in September.

Activity 2.2.2
CMI, VSL, UL

A2.2.2 M24 Delay	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

CMI: Absolute measurement of *f*. Argon measurements finalized at -80 °C and -70 °C at different pressures. Last measurements at -60 °C and data analysis underway.

VSL: Measurements of enhancement factor in N_2 in the temperature range from -60 °C to -40 °C up to 1 MPa have been completed. Data analysis is underway. Relative measurement of *f*.

UL: Experimental data of enhancement factor in N_2 and Ar in the temperature range from -90 °C to -30 °C up to 1 MPa by the end of September (M28). Relative measurement of *f*.

Activity 2.2.3
CEM, VSL, UVa

A2.2.3 M18 OK	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

CEM: 8 humid H_2 gas cylinders sent to VSL for analysis (5, 10, 15, 80 ppm).

VSL: Analysis on H_2 cylinders sent by CEM.

UVa: H_2 cylinders received

Activity 2.2.4
UVa, INTA

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

Delay

UVa+INTA: The new saturator, borrowed from INTA, is in use. Tests with nitrogen conducted instead of argon. By the end of September measurements of *f* in Argon. Absolute measurement of *f.*

Summary - *f* measurements

Enhancement factor data that will be available

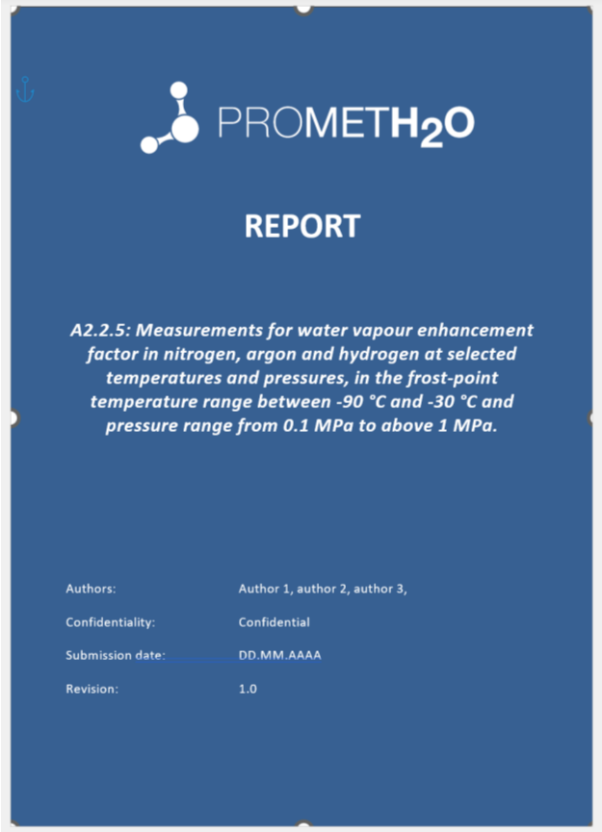
VSL: Between -60 °C and -40 °C up to 1 MPa in N_2.

CMI: Down to -80 °C up to 0.8 MPa in N_2 , some points in Ar.

UL: Between -90 °C to -30 °C up to 1 MPa in Ar/N_2.

UVa: Down to -40 °C up to 1 MPa in $Air/H_2/Ar/N_2$.

CNAM: Between -70 °C and -20 °C up to 0.186 MPa in Ar.



M27 - AUGUST 2023

Delay

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

CNAM: Preparation of a report collecting new enhancement factor data to be used for the validation of equation (A2.3.2). **CNAM sent a table of content to the partners.**

Final draft due by 21 SEPT 2023 – v3

No data are present in the report

Initial contributions from: CEM, CNAM, UL, VSL

Missing: CMI, UVa, INTA

Recommendations provided by VTT about the information and data needed from partners

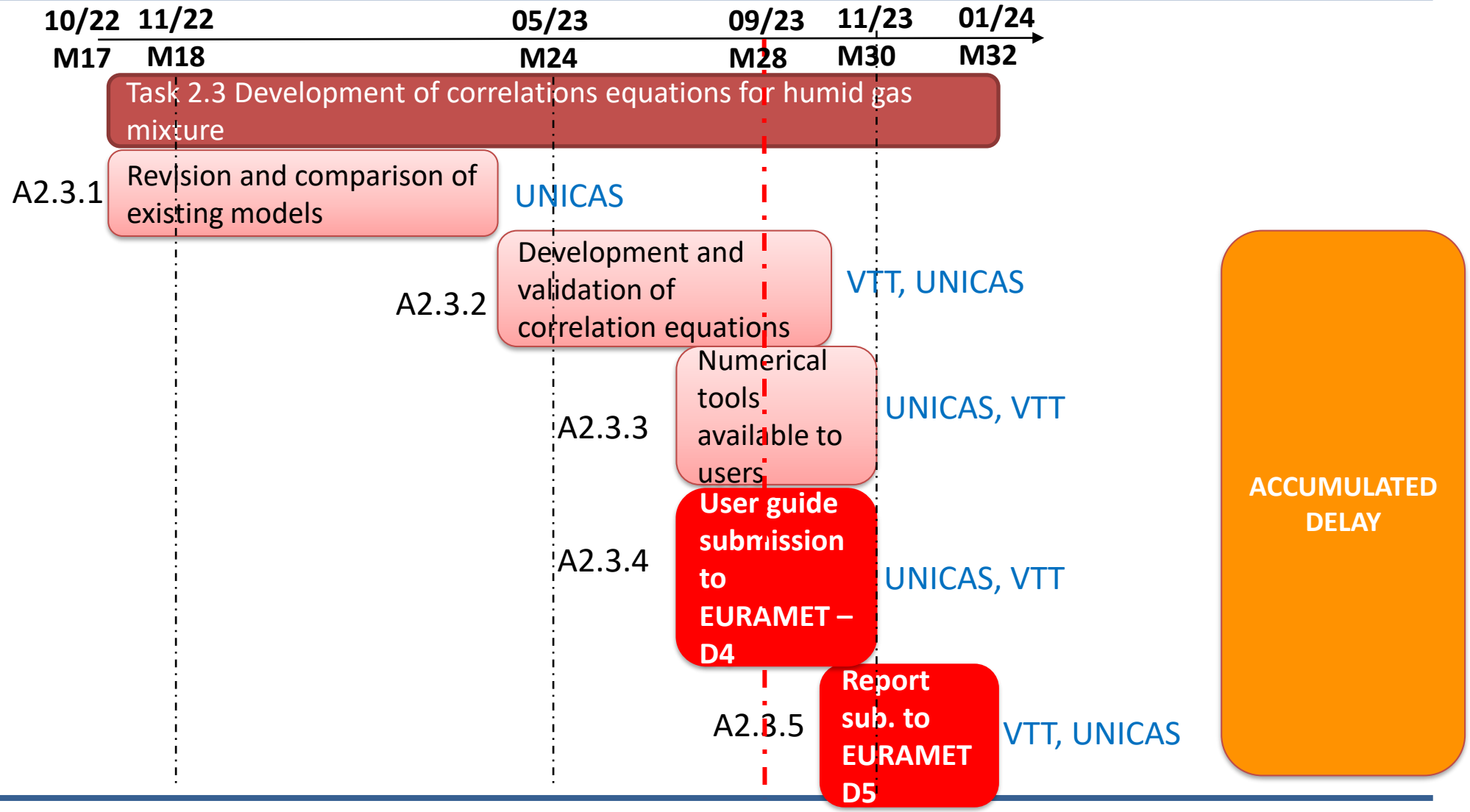
Email sent by VTT on September 4, 2023

- **Status of Measurements**: Please provide an update on the status of your measurements. Indicate if this is already finished, is in the process of finishing, or you cannot complete the measurements timely.
- **Essential Data Parameters**: Please provide at least the following but include more parameters if they are available and relevant: Dew/Frost Point (Tdp/fp) - Total Pressure - Mole Fraction - Conversion Equations: If utilized, ensure to provide the conversion equations. It would be beneficial if links to the equation numbers are supplied, referencing the report of activity A2.3.1.
- **Data Description**: As previously agreed, each partner is kindly requested to provide:
  A brief description of their data headings.
  The general method employed for data acquisition.
  Uncertainty levels associated with the data.
- **Uncertainty Budget:** Each partner should also provide a provisional uncertainty budget. This step will be instrumental as we delve deeper into understanding the details and ensuring precision in our correlation equations.

Kindly ensure that the aforementioned data and information are shared by the **4th of October**.

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

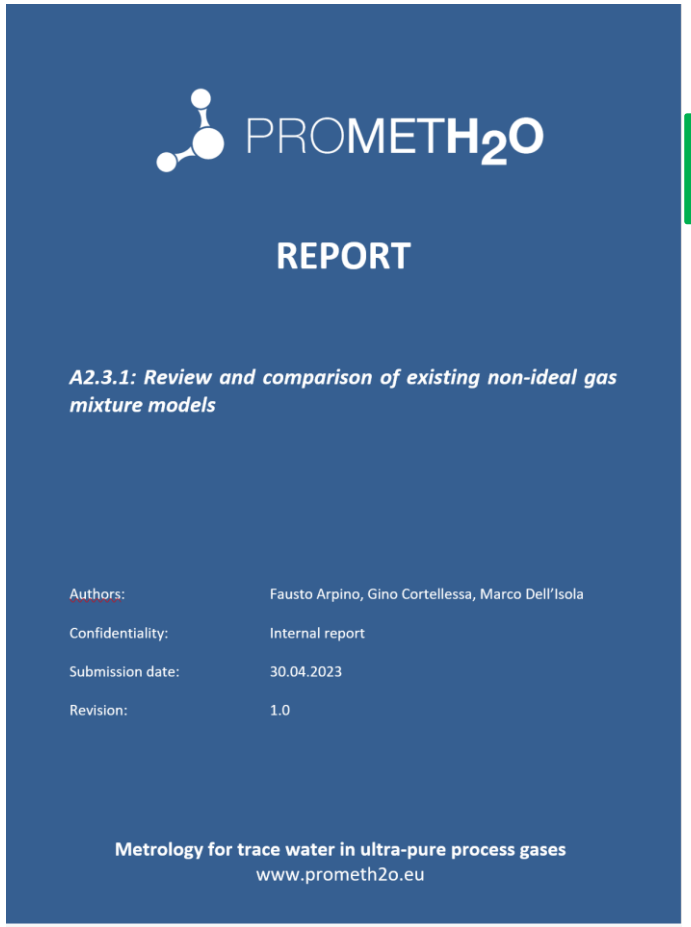
Task 2.3: Activities



Activity 2.3.1
UNICAS

Activity number	Activity description	Partners (Lead in bold)
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**

OK



UNICAS:

A review activity of the scientific literature about the non-ideal humid gas mixture models with reference to hydrogen, argon and nitrogen is completed, as well as a collection of available water vapour enhancement factor measurements in selected gases in the frost-point temperature range between -90 °C and -30 °C at selected pressures from 0.1 MPa to above 1 MPa (**Delayed M28 – September 2023).**

Activity 2.3.2 and 2.3.3
UNICAS, VTT

Not in delay if report A2.2.5 completed by Oct 4

A2.3.2 M29 Delay	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 Delay	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

UNICAS, VTT:

- The measurement data obtained must be added to existing knowledge derived mainly from the literature review. The aim would be to use all available information for correlations.
- What is obtained from this project would be added to the existing information to advance beyond the current state-of-the-art. It is also essential to review the data sets available in the publications and try to have them digitally.

Activity 2.3.4 and 2.3.5
UNICAS, VTT

Delay	A2.3.4 M30	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 N_2, Ar and H_2 in the temperature range between -30 °C and -90 °C and pressure range from 0.1 MPa to above 1 MPa.'*	**UNICAS**, VTT
Delay	A2.3.5 M32	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 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.'*	**VTT**, UNICAS

- **Need to quantify the delay**
- **Do we need to ask to MSU to postpone the delivery date of D4 and D5?**

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Thank you for your attention

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