PROMETH$_2$O

20IND06 PROMETH2O

Metrology for trace water in ultra-pure process gases: goals and challenges

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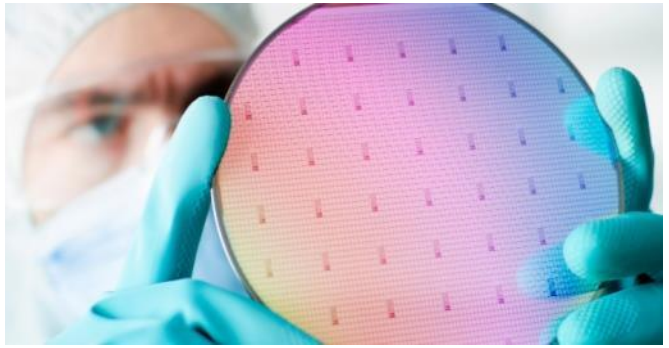
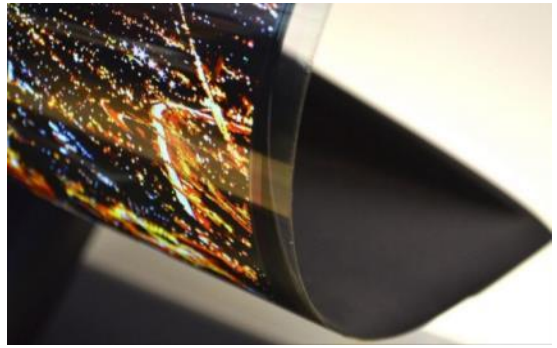
EMPIR EURAMET
The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Identified needs

Semiconductor manufacturing - demands for UHP process gases with total impurities as low as few ppb.

Organic electronics - highly moisture-sensitive, needs ultra-dry manufacture and vapour barrier coatings.

UHP bulk process gases - need to be manufactured with total impurities below 1 ppm in volume (grade N6.0 or better).

Utility power generation - needs dry hydrogen (<5 ppm) to cool high-efficiency stationary generators.

Instrument manufacturers - need traceable standards to support their product development while end-users rely on them for instrumental testing and calibration.

Project challenges

Water vapour is the single largest matrix contaminant in ultra-high purity (UHP) process gases used in key technology areas.

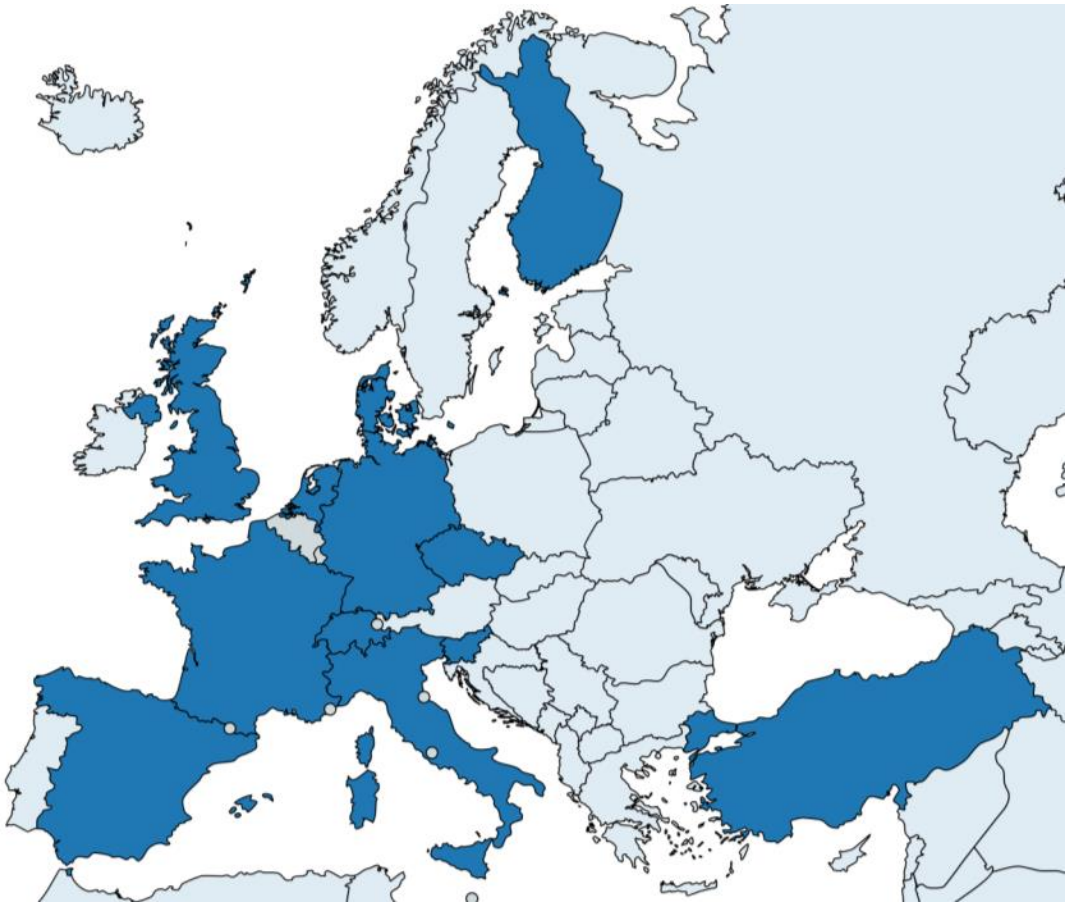
Its measurement presents **great challenges to both gas manufacturers and analytical instrument makers**.

- **To fill the gap** between the demand of traceable measurement and the available humidity standards currently limited at ~1 ppm.
- **To develop traceable and improved methods** for trace water measurement relevant to the production and use of UHP gases.
- **To facilitate the uptake of the technology** by the gas industry supply chain through exploiting knowledge and services developed in an European-wide metrology infrastructure.

PROMETH2O **objectives**

- ✓ **New measurement methods** in the amount fraction range between 5 ppm and 5 ppb with relative standard uncertainty between 3 % and 8 %.
- ✓ **New primary standards** for trace water vapour in N_2, Ar and H_2 down to 5 ppb (or -105 °C frost point temperature) at pressures up to 1 MPa.
- ✓ **New data** and correlation equations of water vapour enhancement in N_2, Ar and H_2 in the temperature range from -30 °C to -90 °C and pressures up to 1 MPa.
- ✓ **Demonstration** at selected industrial settings with real-time measurements and on-site calibrations.
- ✓ A **toolkit of metrological solutions** for robust measurement traceability in the production of ultra-pure process gases, by leveraging on improved standards and range-extended measurement capabilities.

The Consortium



19 partners from 12 countries → 240 person-months

Project implementation - Month 9

Stakeholder's Steering Board

Robust traceability by suitable primary standards

Improved trace water measurement methods

Improved knowledge of real humid gas mixtures

Creating impact

Demonstration at two industrial t
Facilitation of end-user upta

Improved trace water measurement methods and techniques

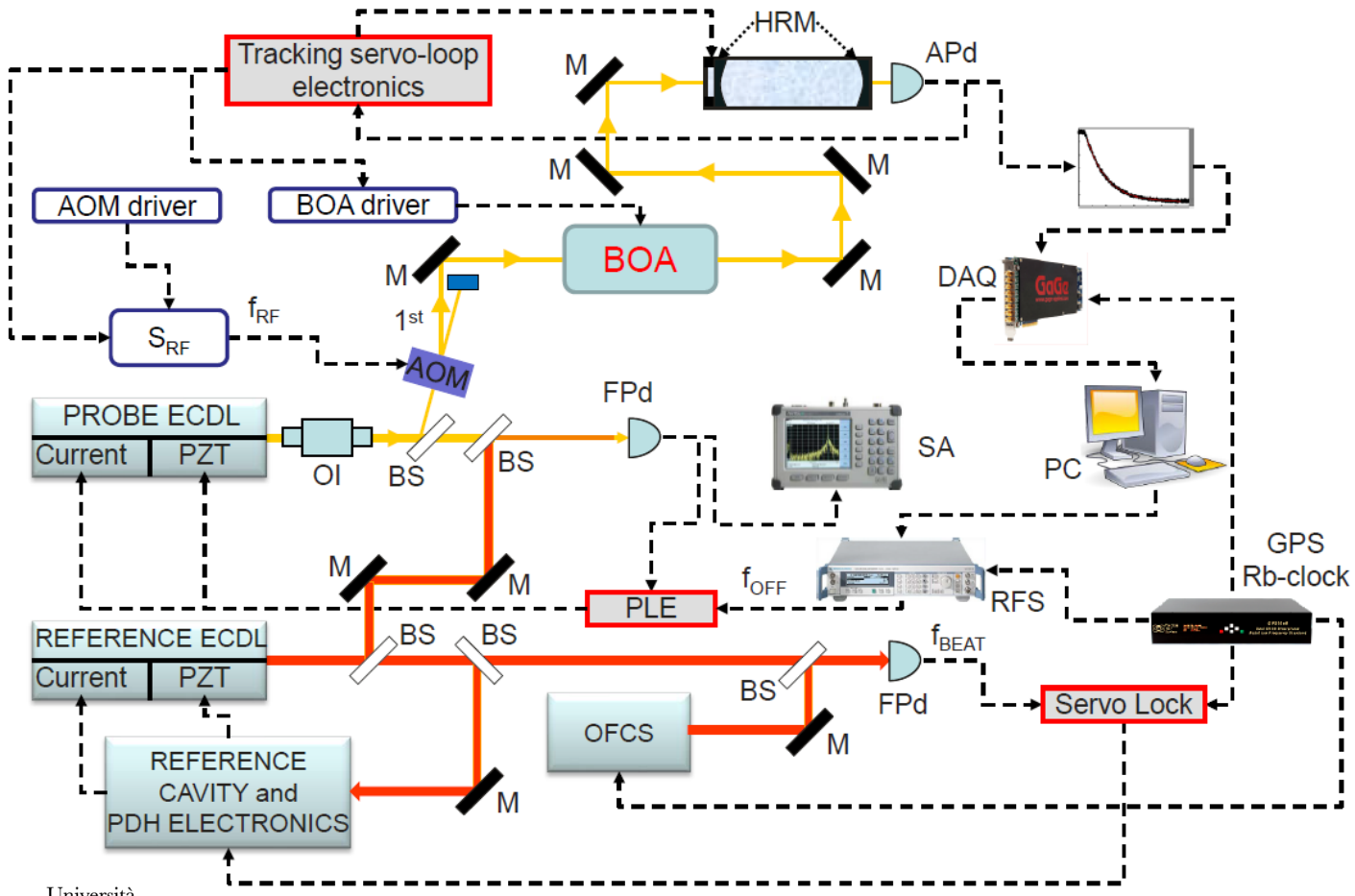
❖ Development and improvement of optical analysers

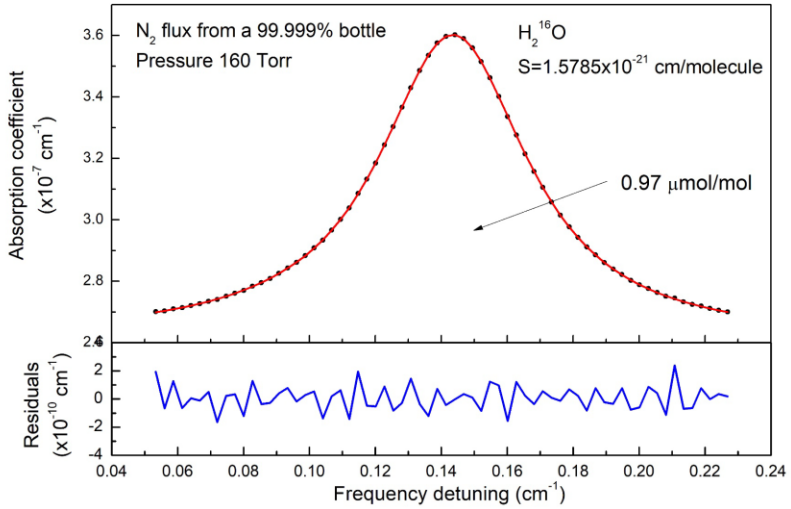
- Target: **H_2O traces in Ar, N_2, H_2** [from 5 ppm (-65 °C) to 5 ppb (-105 °C) @ 0.1 MPa].
- Relative uncertainty: 3 % (at 5ppm) to 8 % (at 5 ppb)

❖ 4x systems

- ❑ Enhancements in NIR comb-calibrated frequency-stabilized cavity ring down spectrometer (CC-FS-CRDS);
- ❑ NIR cavity-enhanced frequency modulated (CE-FM) spectroscopy hygrometer development;
- ❑ Far-UV absorption spectroscopy system development;
- ❑ Upgrade of existing high-resolution FTIR system.

NIR comb-calibrated frequency-stabilized cavity ring down spectrometer (CC-FS-CRDS)





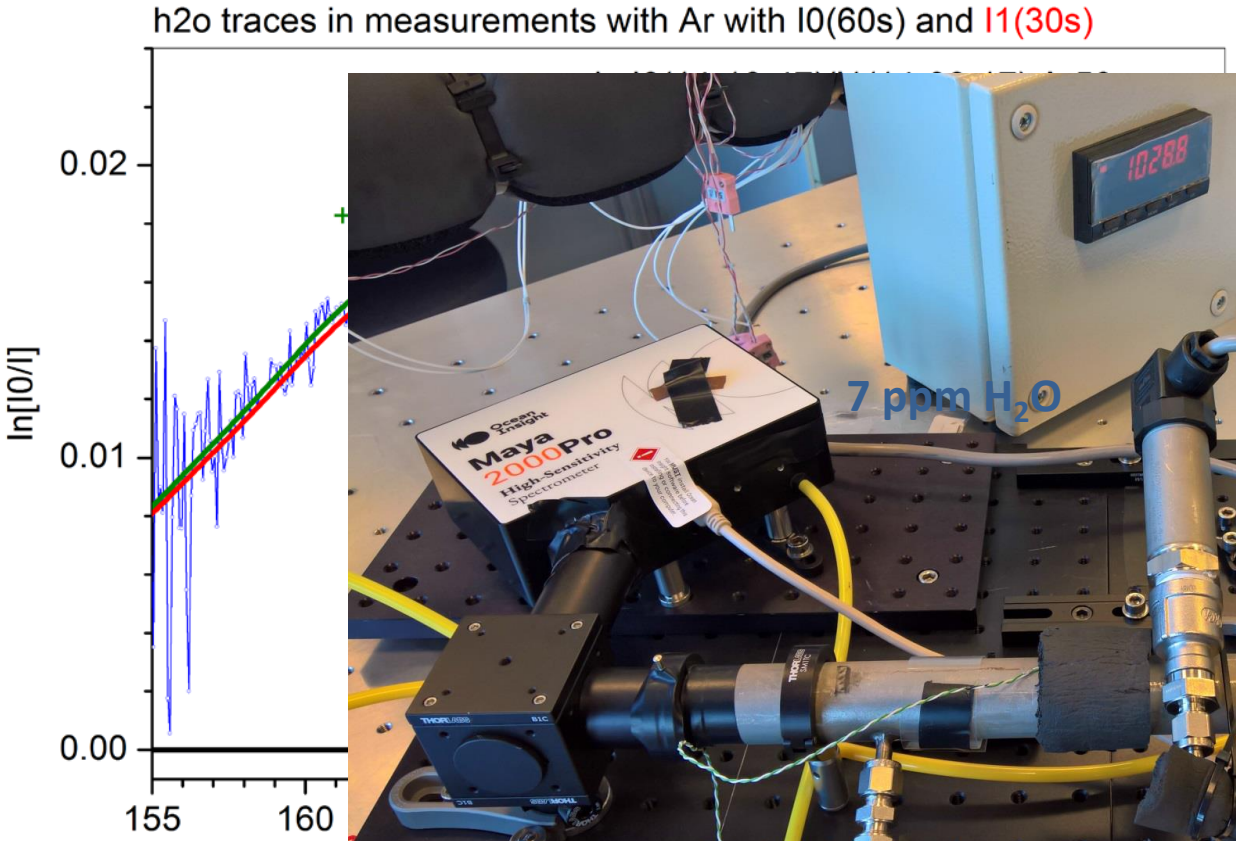
SI traceable uncertainty of 0.3% for line intensity

Contribution	Type A	Type B
(k=1)	(%)	(%)
Statistical	0.5 - 3	
Line strength		0.3
Frequency scale		Negligible
Line shape model		0.1
Gas temperature		0.05
Partition function		0.04
Pressure		0.1
Overall combined uncertainty	0.5 – 3.1 %	

Università degli Studi della Campania *Luigi Vanvitelli*

A compact and transportable far-UV system

H_2O Cross section



Initial experiments

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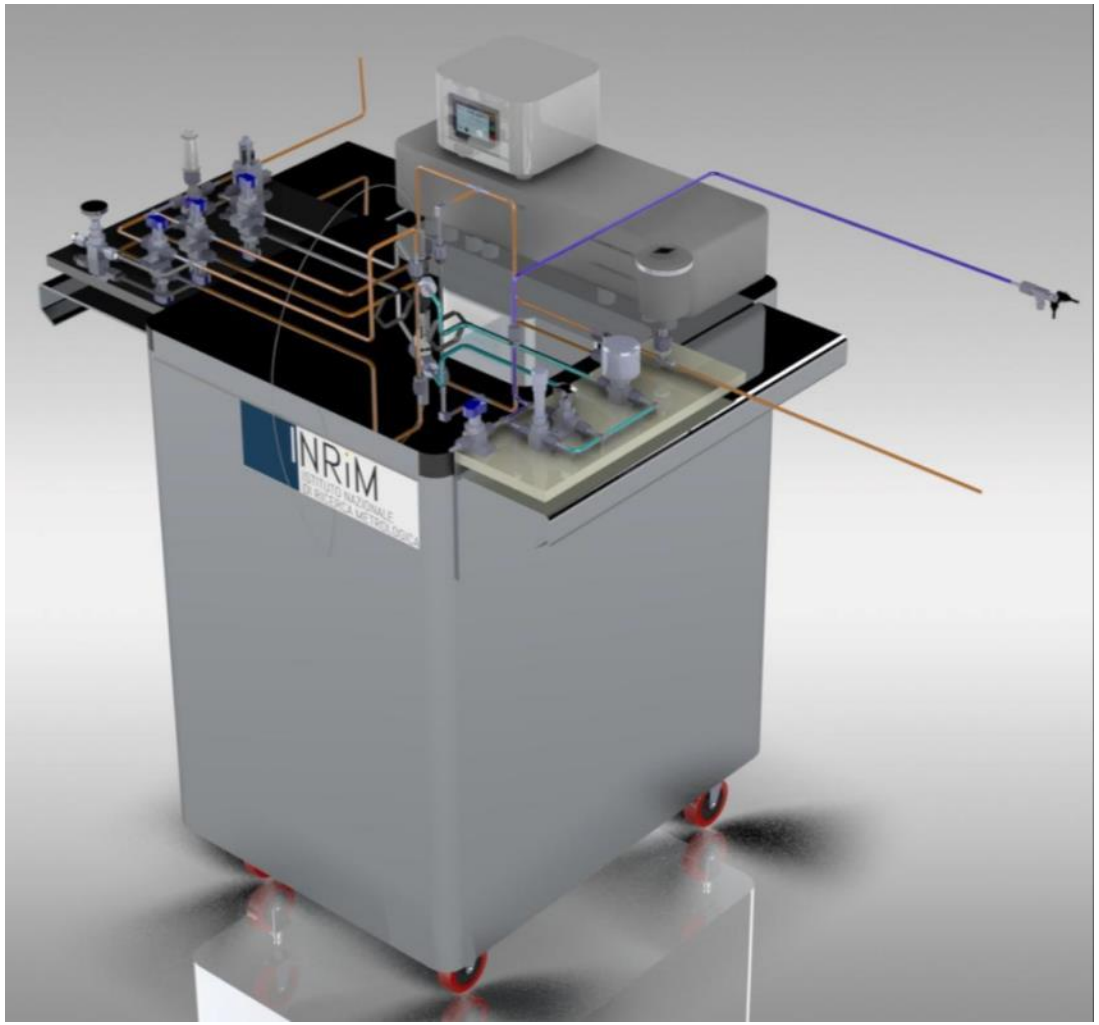
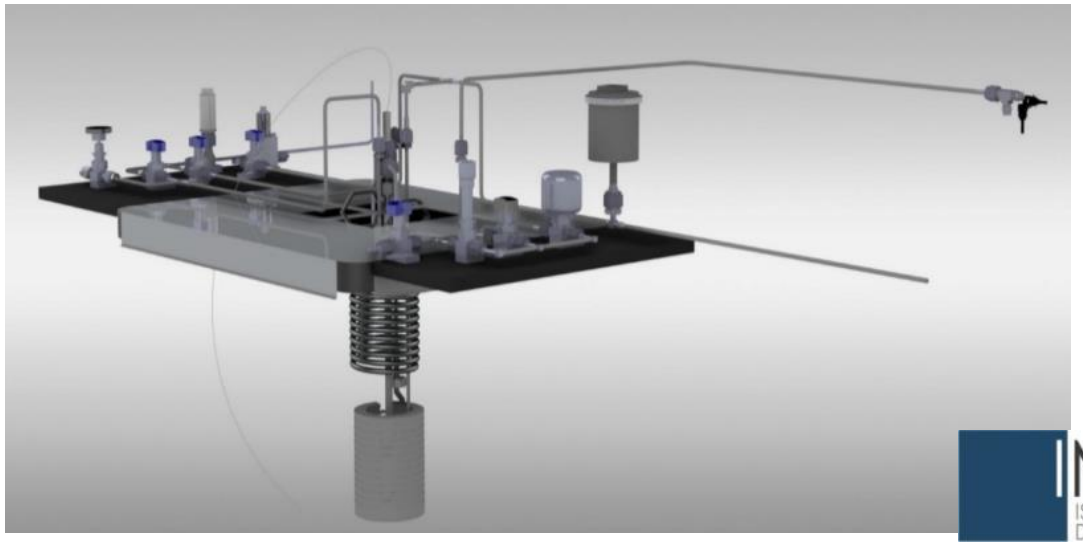
Robust traceability to trace water measurements in real humid gas mixtures



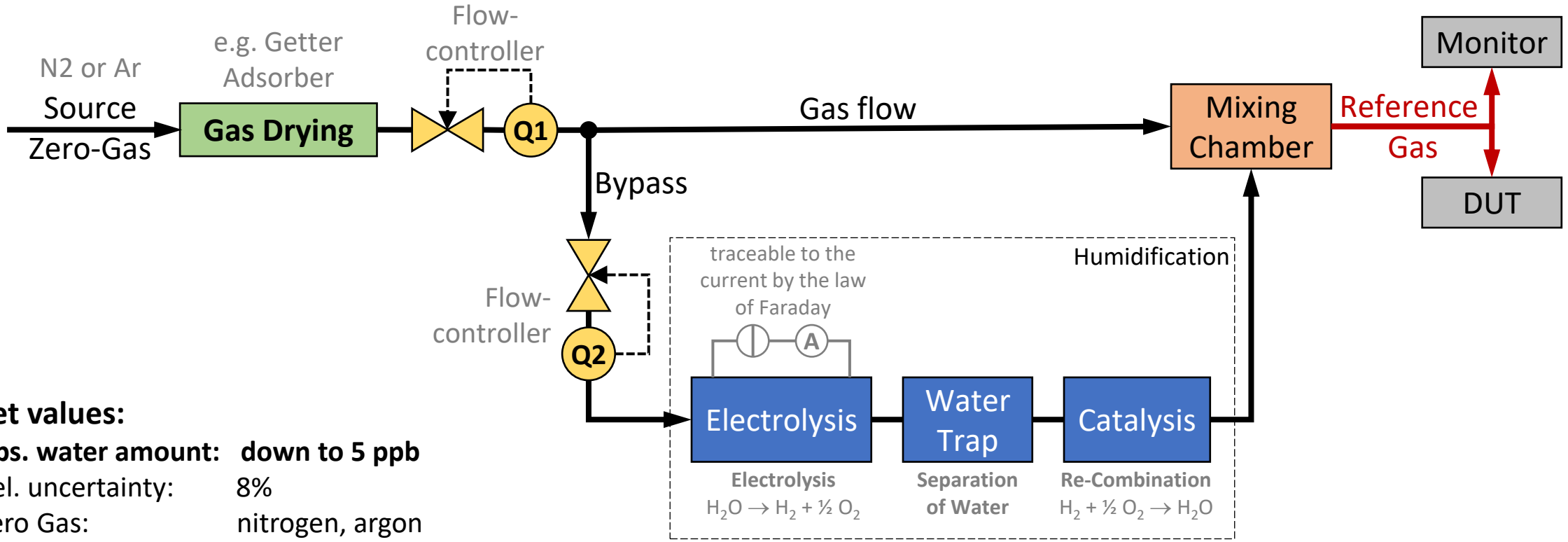
Range extension of the INRiM LFP generator

- Two-pressure, single-pass, humidity generator
- **Frost-point temperature between -105 °C and -20 °C**
- W.V. mole fraction between 5 ppb_v and 1038 ppm_v
  Pressure: 200 hPa to 6000 hPa
- Carrier gas: Nitrogen, Argon



INRiM
ISTITUTO NAZIONALE
DI RICERCA METROLOGICA

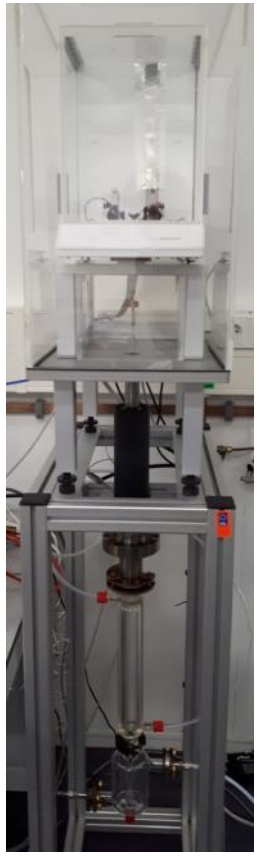
Basic setup of the PTB Coulometric Trace Water Generator



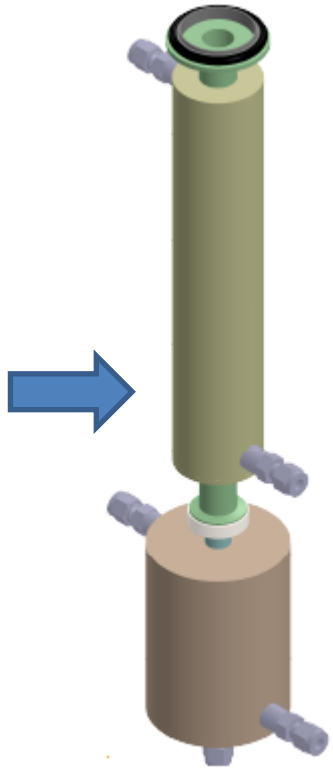
Target values:

- **Abs. water amount:** **down to 5 ppb**
  Rel. uncertainty: 8%
- Zero Gas: nitrogen, argon
  Abs. uncertainty : less then ±3 ppb

Permeation system based on a passivated magnetic suspension balance



Previous design



New 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: 50 nmol/mol up to 5 µmol/mol
Matrix gases: N_2 and H_2

Current testing and validation of the new system

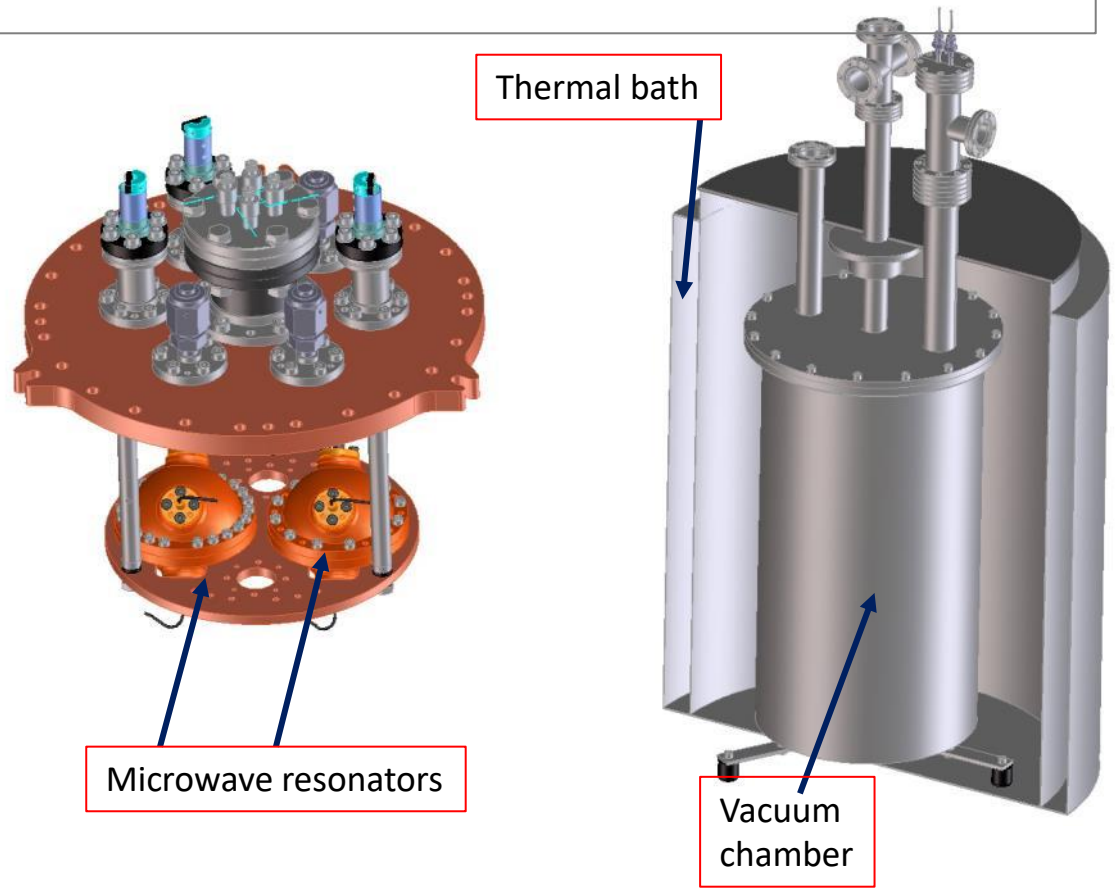
New chamber

Measurement of the enhancement factor in selected humid gas mixtures

Goal: to improve the 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 new microwave-based hygrometer

- Design of the new microwave hygrometer system operating to a pressure of 7-10 bar
- Completed the design of the new system (microwave resonators, the pressure vessel, the thermal shield and the vacuum chamber).
- The manufacturing procedure and the purchase process are in progress.



Transportable Frost Point Generator

Achievements so far:

- Transportable frost point generator
- Flow rates 1-to-5 litre/min on external closed loop
- Generated conditions down to -100°Cfp
- Independent test data down to -90°Cfp

System reproducibility

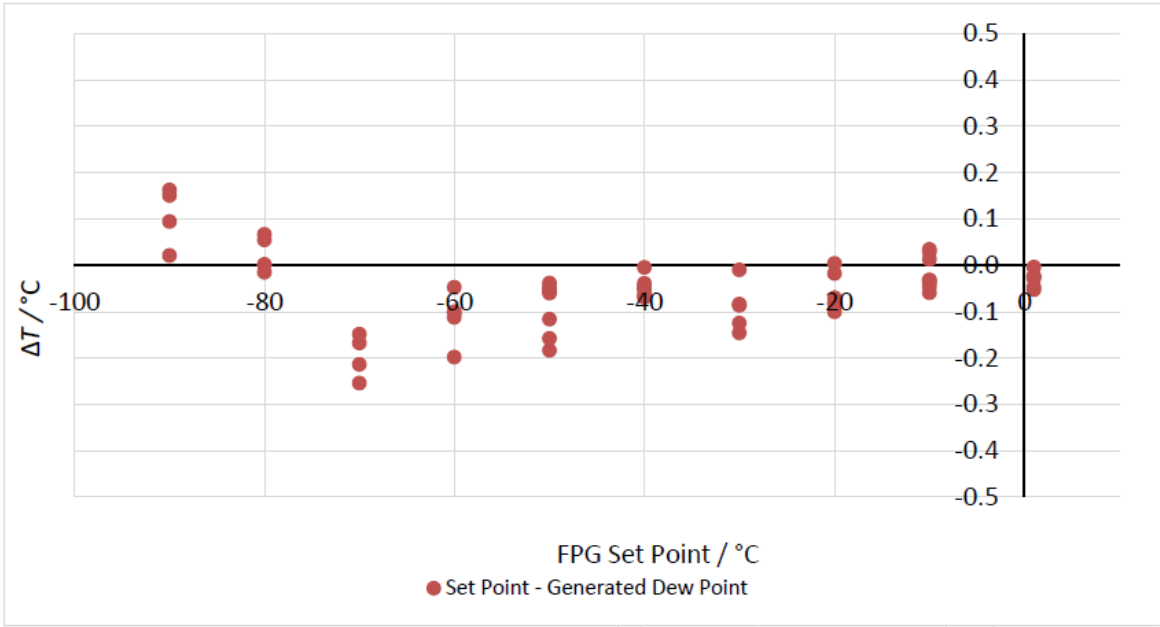


Figure 2: Values of the difference, ΔT, between the FPG Set Point and the Generated dew-point temperature value as measured by a reference chilled-mirror hygrometer at each test point between -90 °C and +1 °C.

Impact on industry and society

Key drivers

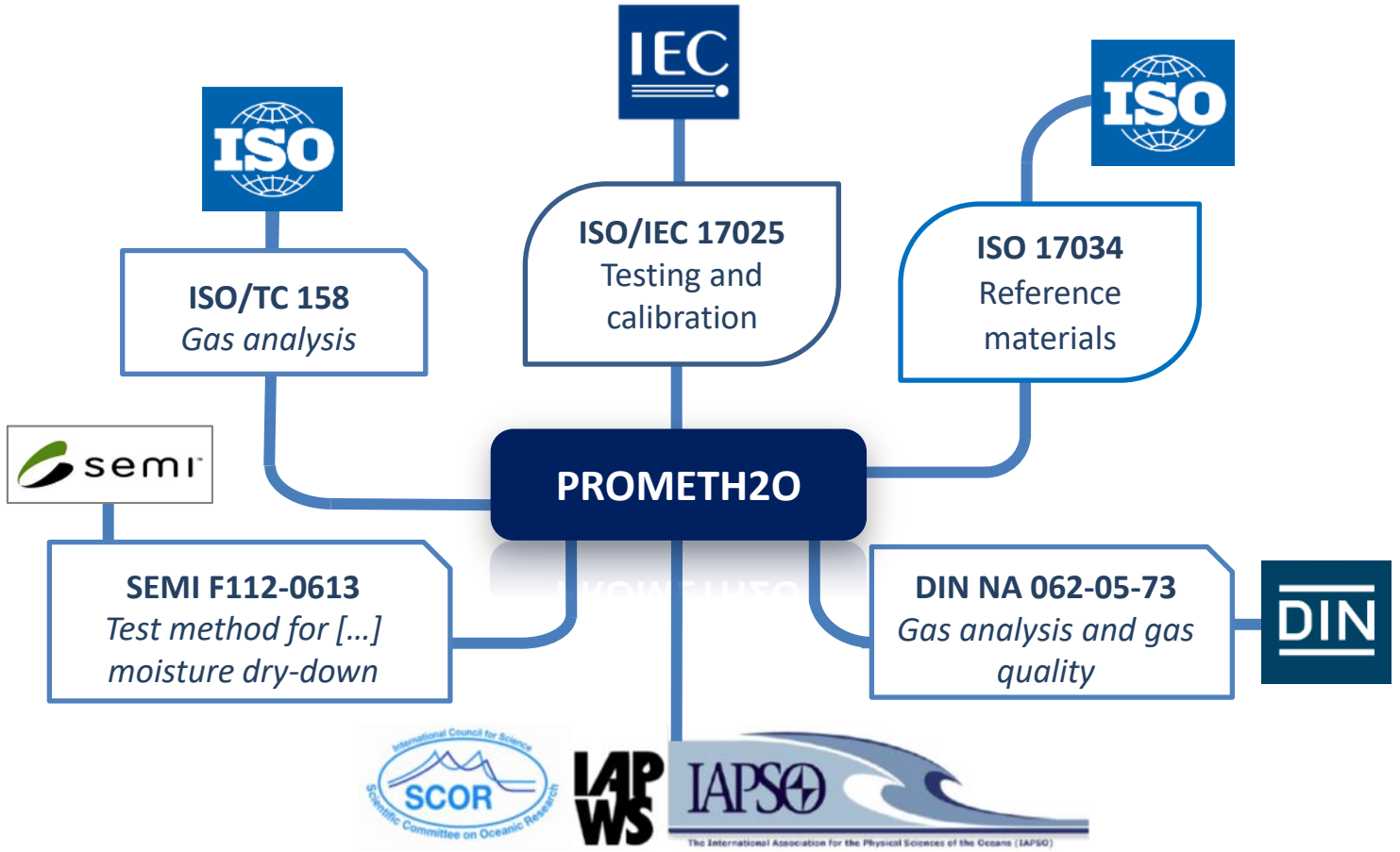
- Global market for industrial gas reached $95 billion in 2019. It grew at 5 % per year.
- In Europe, in 2019, the gas market reached a value of about € 15 billion.
- European PV market is forecast for double-digit yearly growth. It grew by >100 % in 2019.
- OLEDs for next-generation flexible displays – a booming market to be worth $3 billion in near future.

Expected impact

- Early industrial impact expected **on UHP gas manufacturing and supply.**
- **Improved, traceable, measurements** of trace water in UHP gas production and supplies to serve advanced industrial sectors.
- **On site calibrations**/checks using transportable references for improved process efficiency.
- To sustain **innovation and competitiveness** of European instrument makers and service providers.
- To contribute to **renewable and sustainable technologies** – solar, PV, low-energy light sources, etc.

Impact on metrology and standards

- **Extended-range primary standards** and measurement traceability for trace water in UHP gases.
- **Integration of metrology infrastructure** in Europe and leadership of European NMIs in this developing field.
- **Underpinning of metrology** of trace water for wider reference gases (e.g. N_2, H_2, Ar).
- **Better knowledge** of measurement techniques and of real humid gas mixtures.
- A **CIPM key comparison** enabled in the trace water range.



Stakeholders' engagement

A Steering Board (SB) made of key stakeholders, i.e., gas and equipment manufacturers, industry, standards developing organisations, international scientific associations **has been established.**

21 organisations have joined the SB so far

In summary, PROMETH2O will …

- Improve **trace water measurement** methods and techniques **[from 5 ppb to 5 ppm]**.
- Provide **robust traceability** to trace water measurements by developing suitable standards **down to 5 ppb** in N_2, Ar and H_2.
- Improve the present knowledge of **thermophysical data** of real humid gas mixtures.
- Demonstrate improved trace water measurement methods in **industrially-relevant facilities.**
- Facilitate **the take up** of the technology and the European-wide measurement infrastructure.

Upcoming events

GAS Analysis 2022

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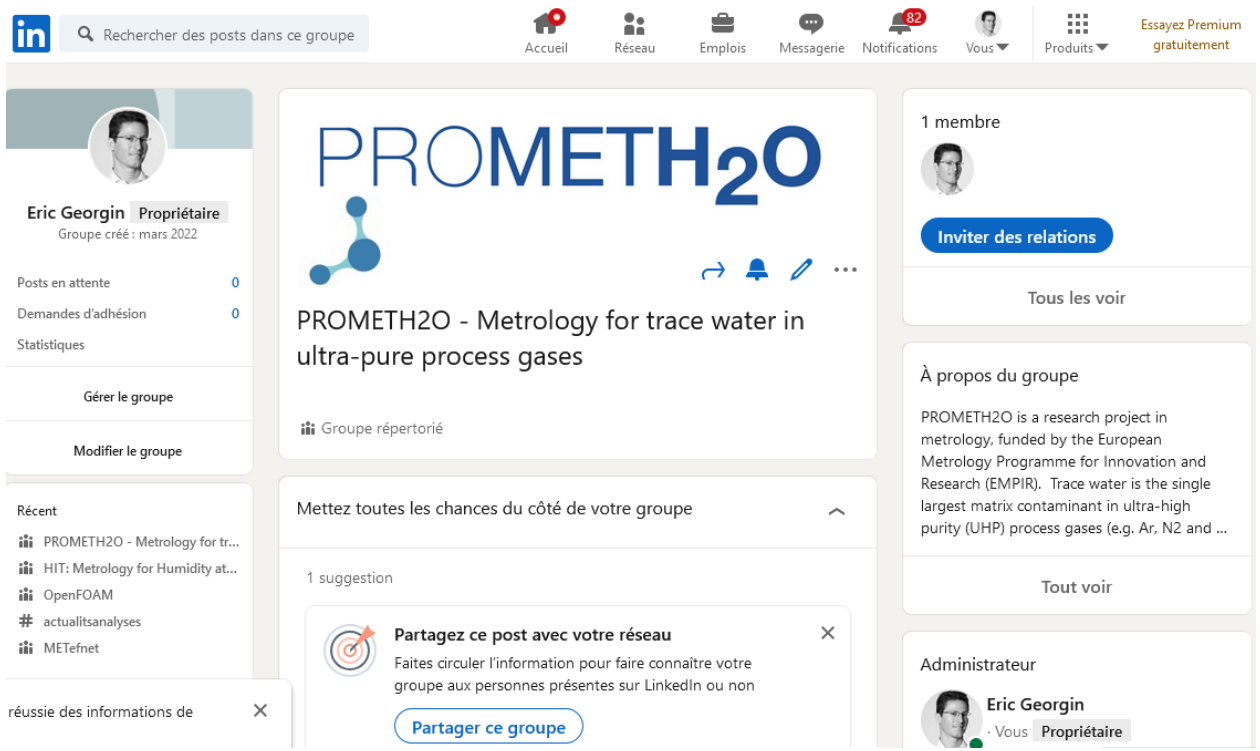
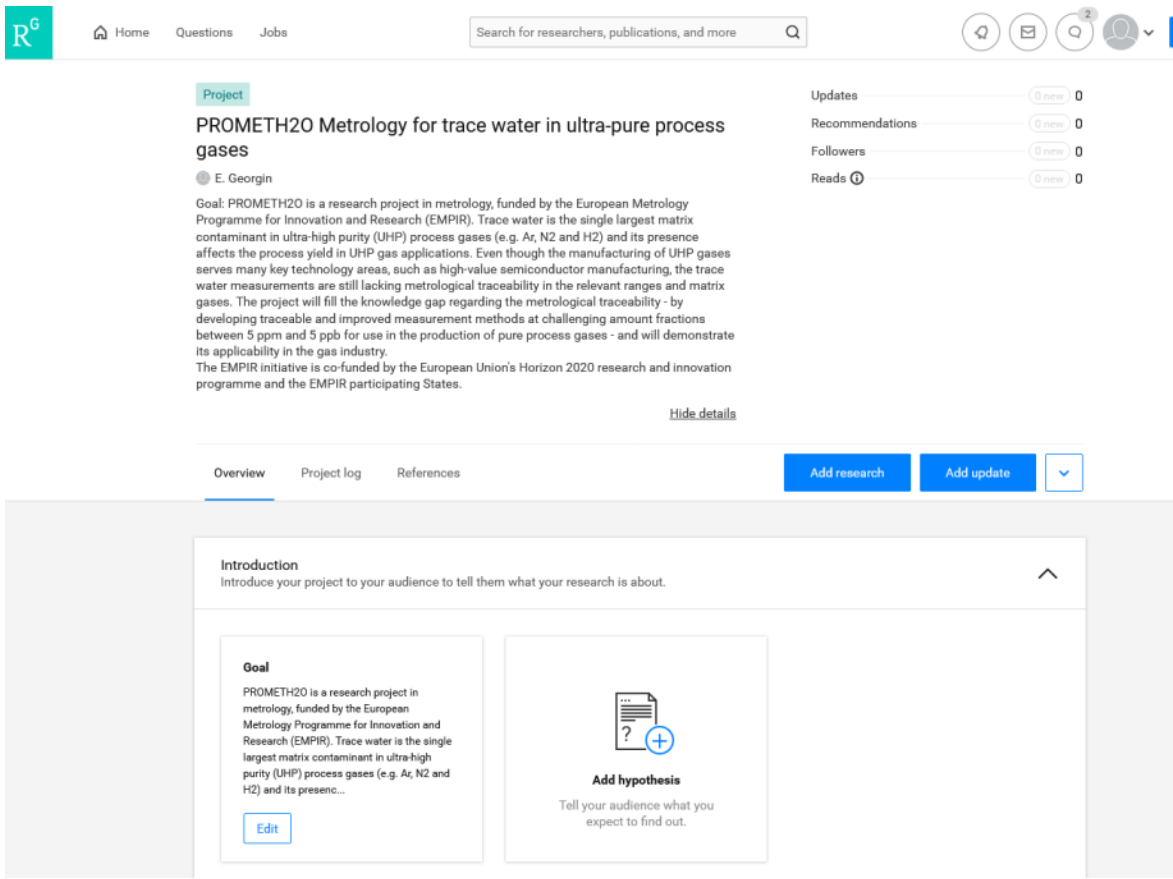


Research gate



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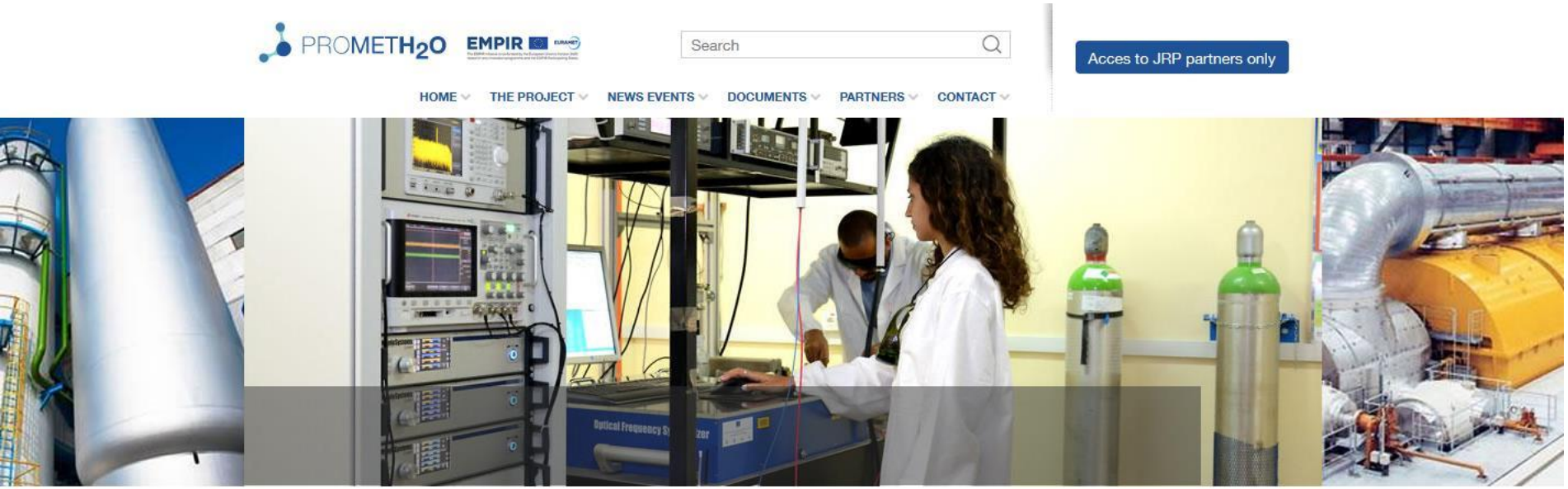

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Thank you for your attention!