PROMETH$_2$O

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

**Vito C. Fernicola, INRIM**

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EMPIR EURAMET

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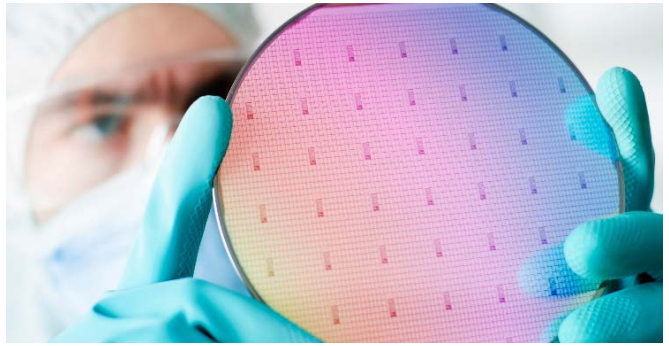
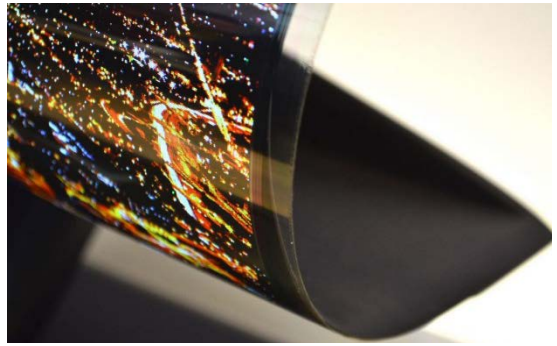
# Identified needs

**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.

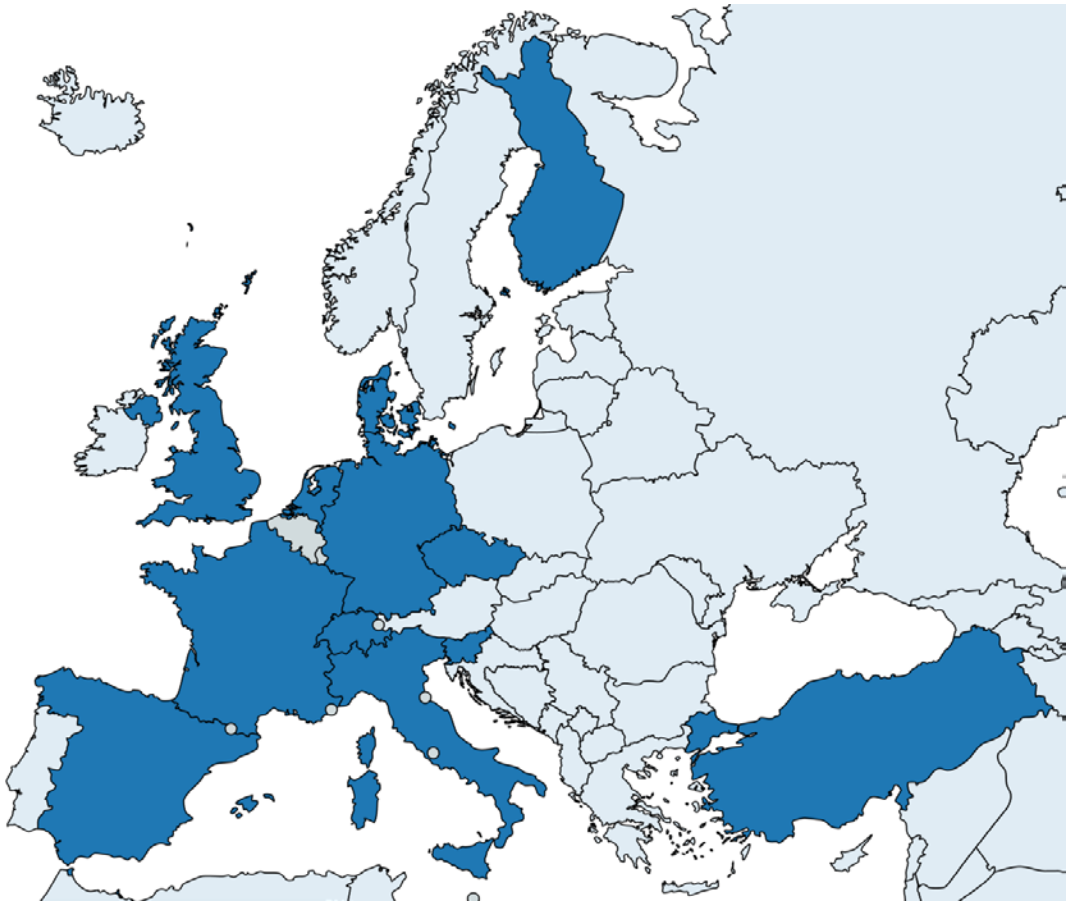
Its measurement presents **great challenges to both gas manufacturers and analytical instrument makers**.

- **To fill the gap** between the demand of traceable measurement and the available humidity standards currently limited at ~1 μmol/mol.
- **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 μmol/mol and 5 nmol/mol 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 nmol/mol (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

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

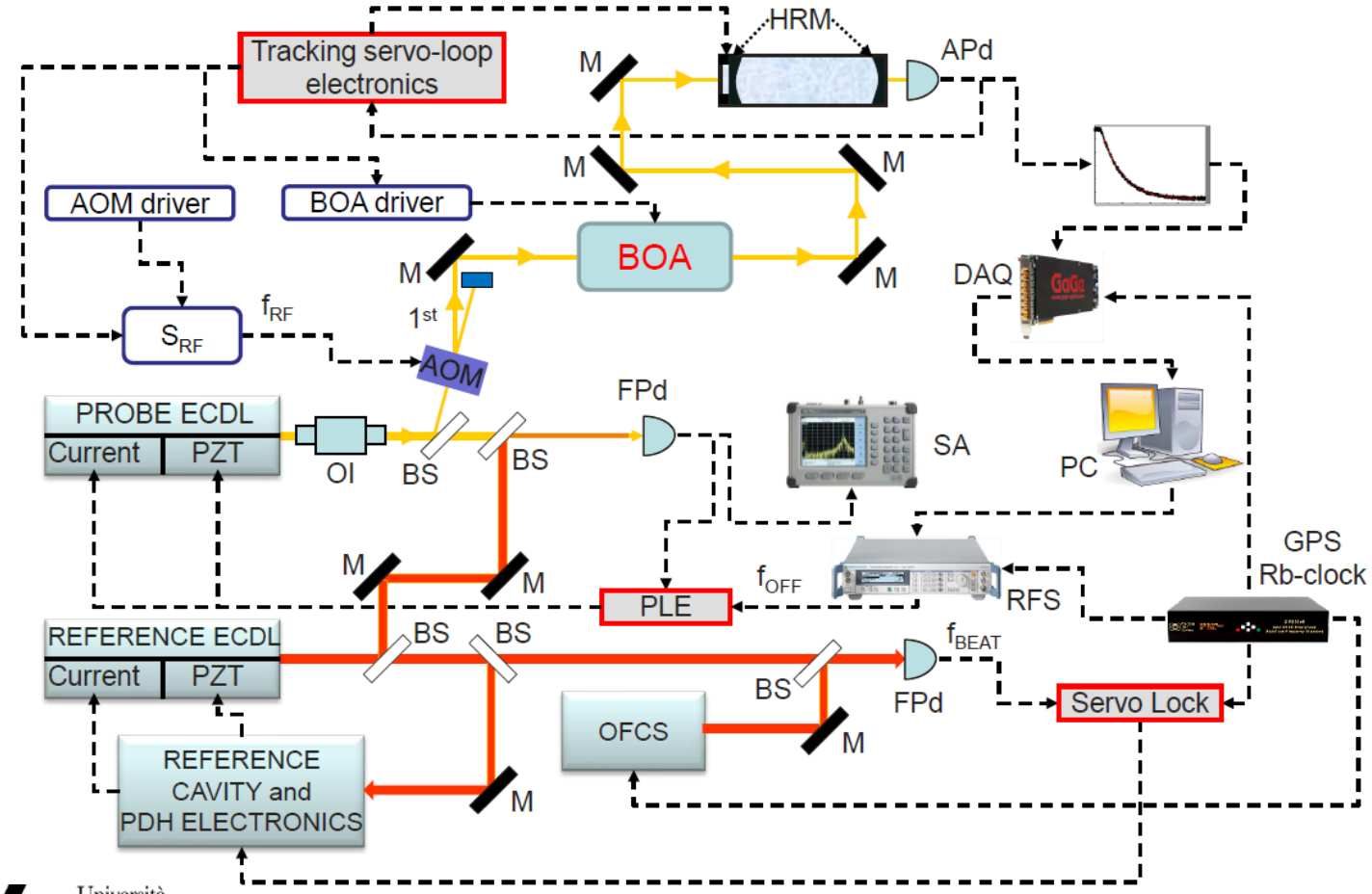
## ❖ Development and improvement of optical analysers

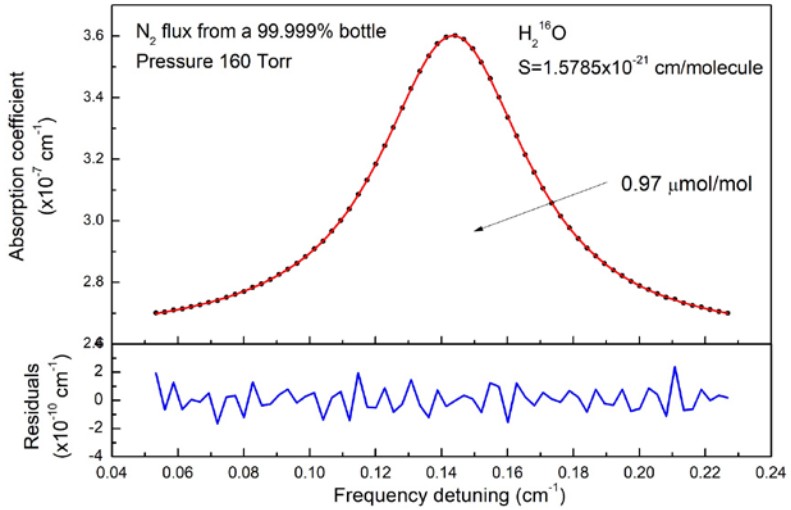
- Target: $H_2O$ traces in Ar, $N_2$, $H_2$ [from 5 ppm (-65 °C) to 5 ppb (-105 °C) @ 0.1 MPa].
- Relative uncertainty: 3 % (at 5 ppm) to 8 % (at 5 ppb)

## ❖ 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)



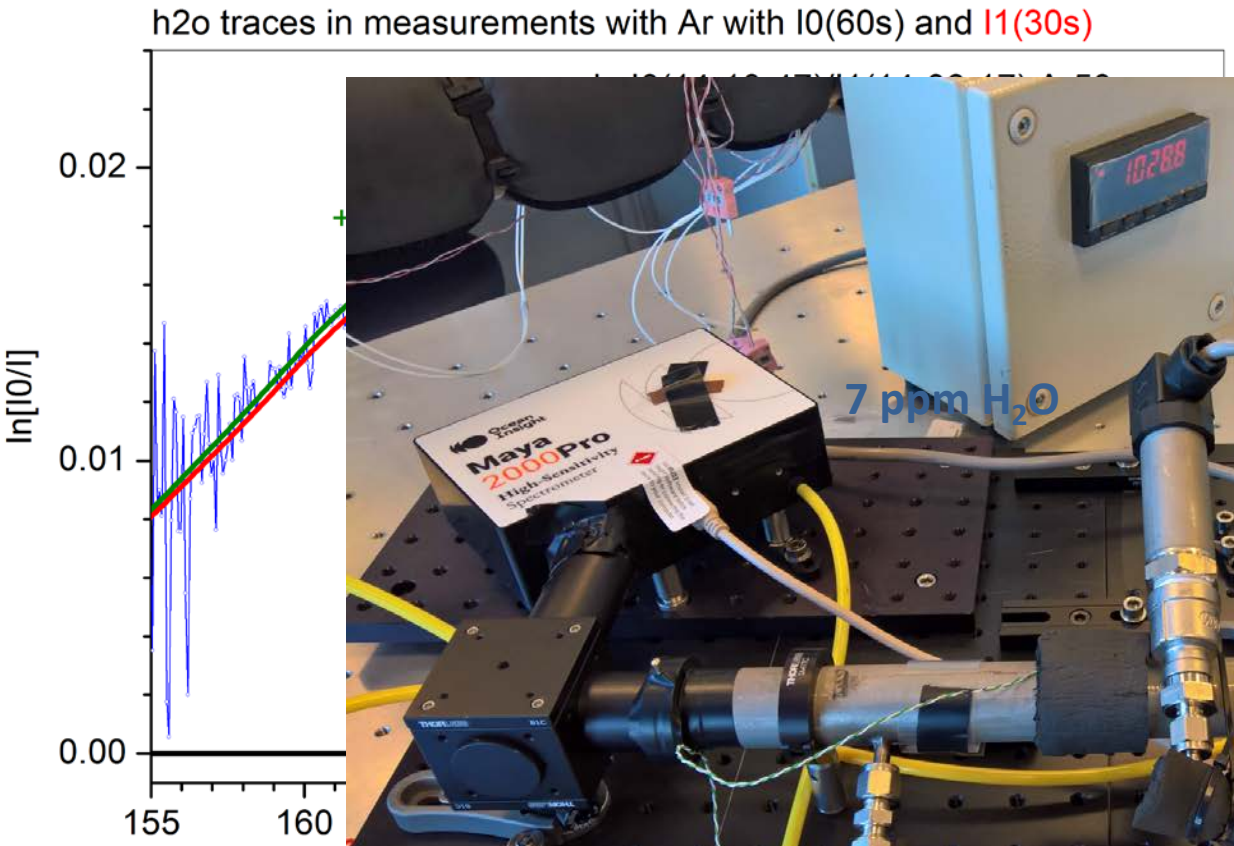

**SI traceable uncertainty of 0.3% for line intensity**

| 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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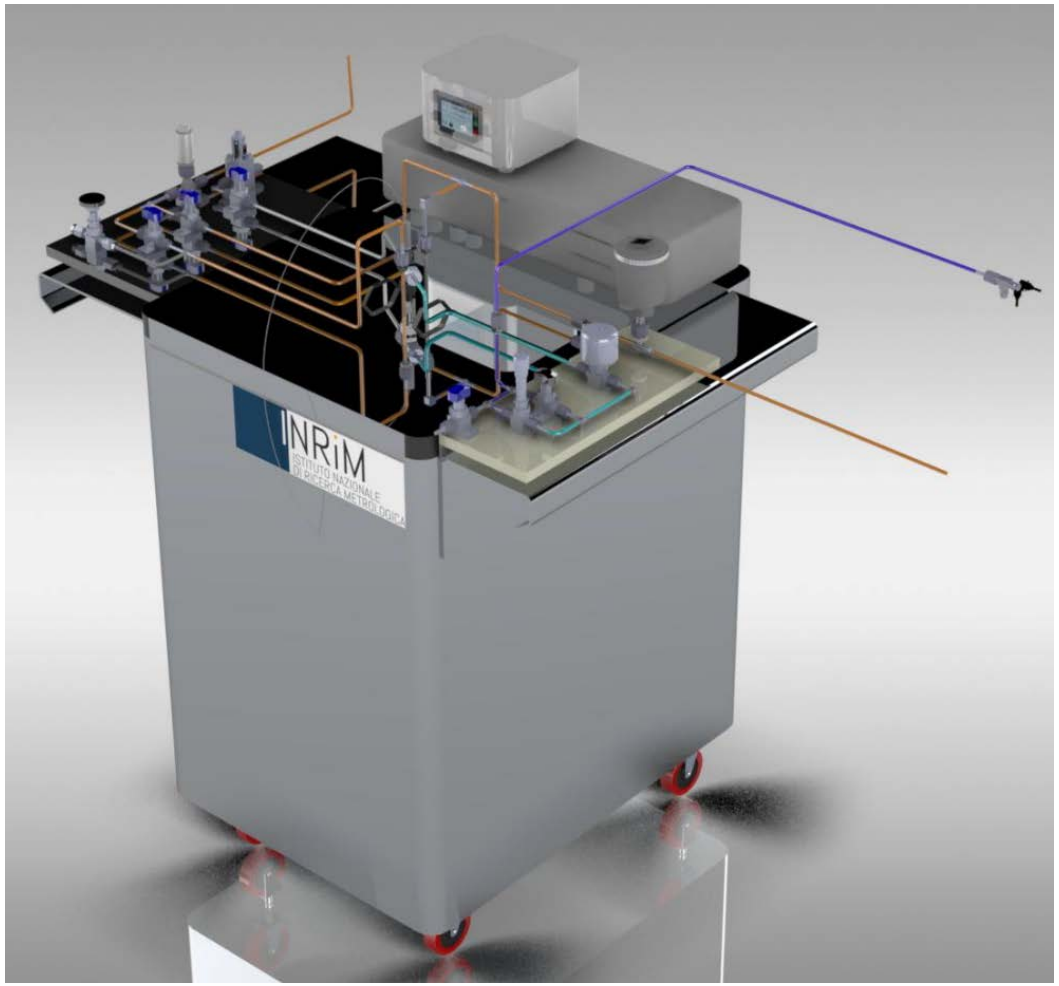
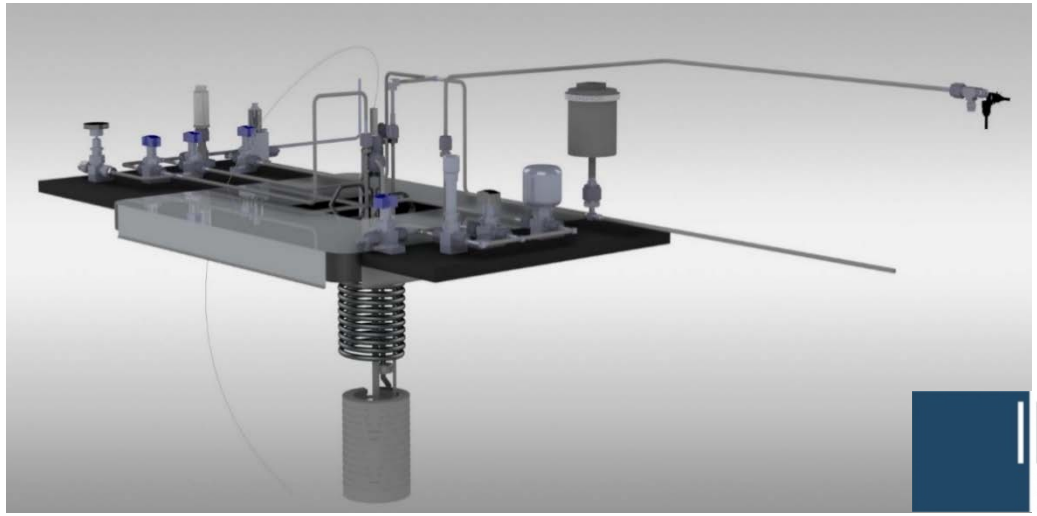
x 100 cm

# Robust traceability to trace water measurements in real humid gas mixtures



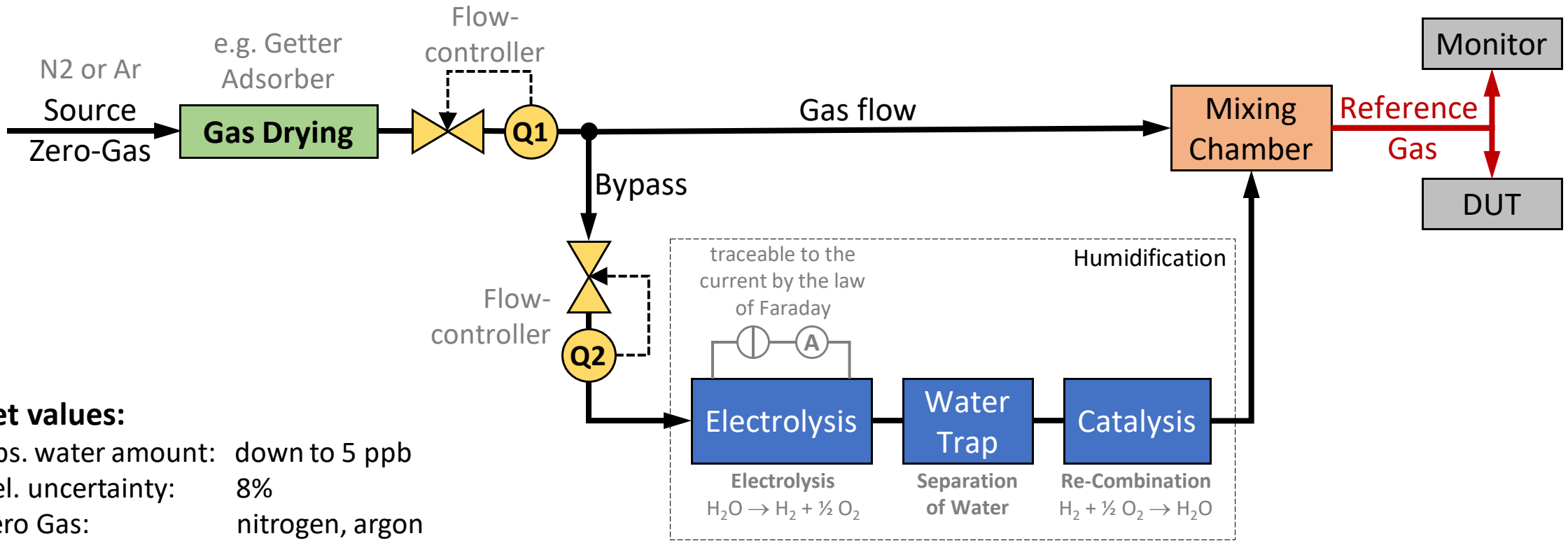

## Range extension of the INRiM LFP generator

- Two-pressure, single-pass, humidity generator
- **Frost-point temperature: -105 °C to -20 °C**
- **Water vapour mole fraction: 5 nmol/mol to 1 mmol/mol**
- Pressure: 200 hPa to 0.5 MPa
- Carrier gas: Nitrogen, Argon



INRiM
ISTITUTO NAZIONALE
DI RICERCA METROLOGICA

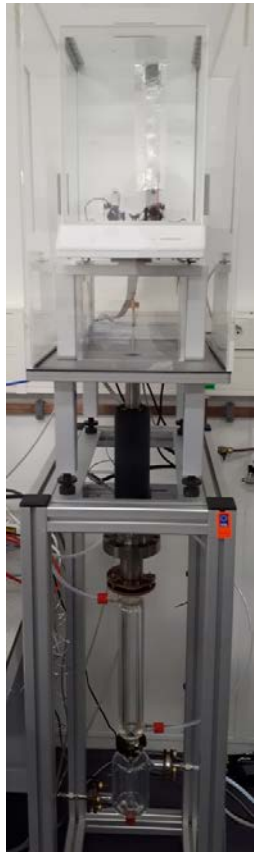
# Basic setup of the PTB Coulometric Trace Water Generator



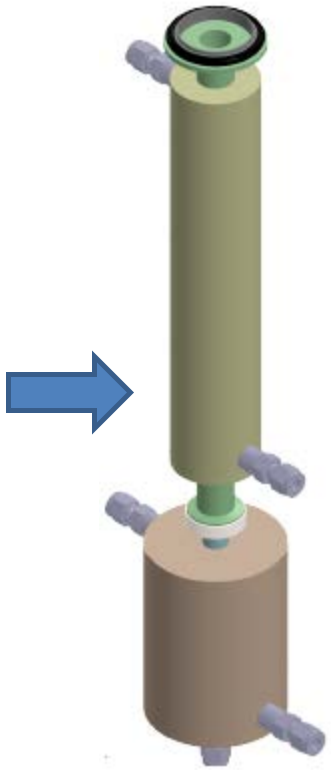

**Target values:**

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

# VSL 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 $H_2$**

Testing and validation of the new system

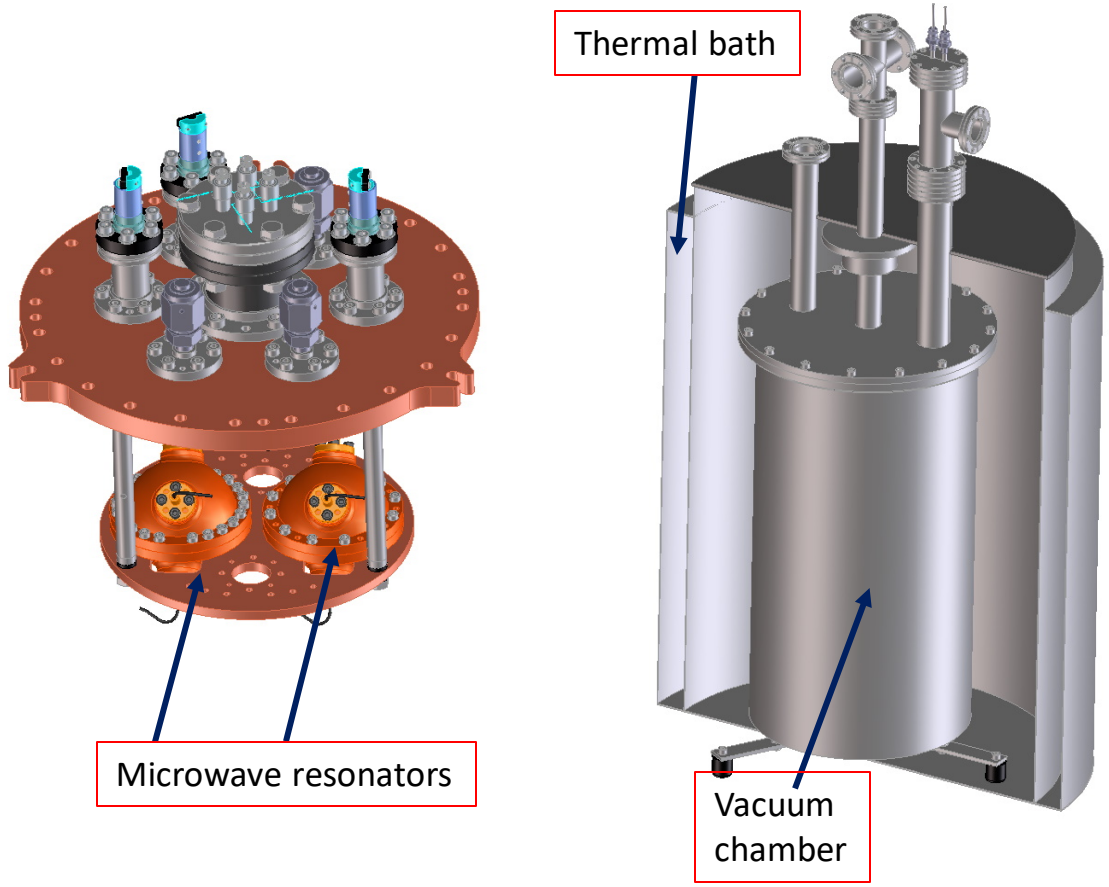
New chamber

# 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 up 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 rate 1-to-5 L/min on external closed loop
- **Generated conditions down to -100°C fp**
- **Independent test data down to -90°C fp**

## System reproducibility

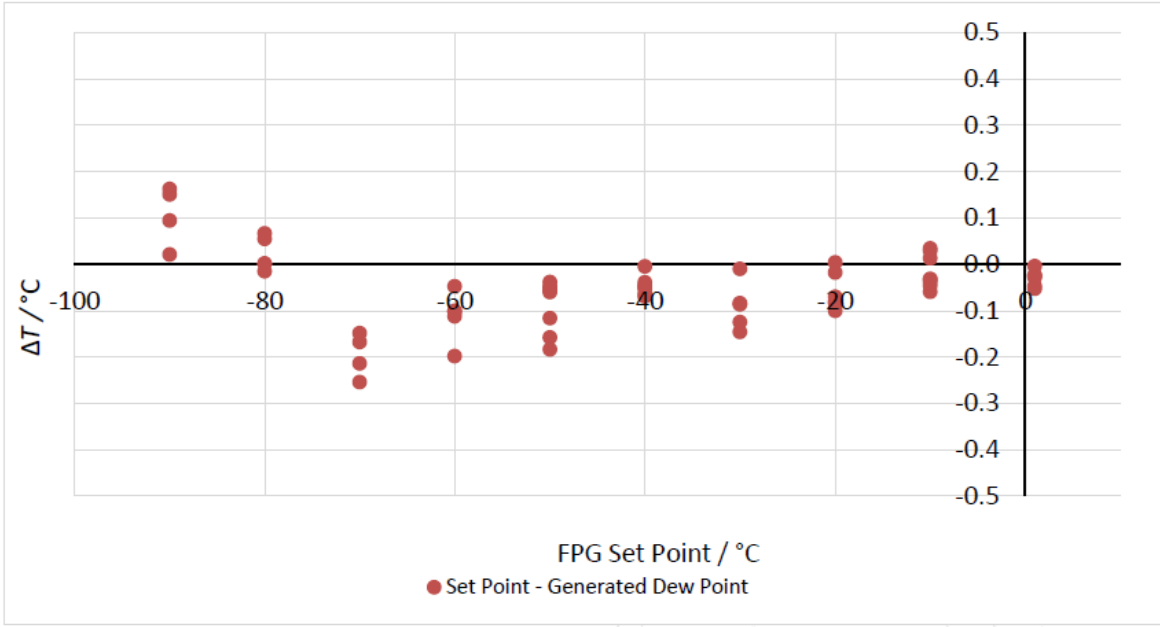



**Figure 2: Values of the difference, *ΔT*, between the FPG Set Point and the Generated dew-point temperature value as measured by a reference chilled-mirror hygrometer at each test point between -90 °C and +1 °C.**

# Impact on industry and society

## Key drivers

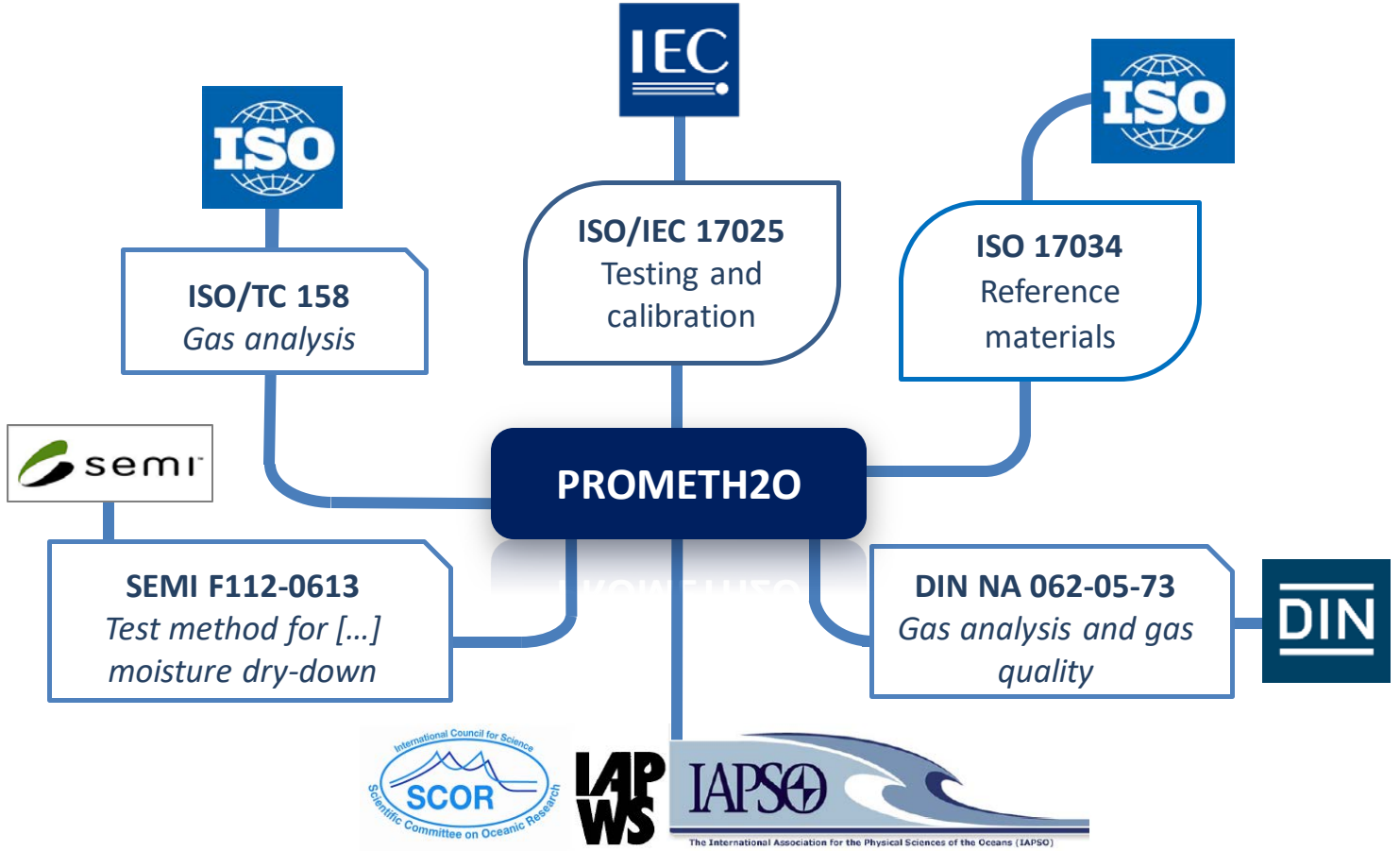
- Global market for industrial gas reached $95 billion in 2019. It grew at 5 % per year.
- In Europe, in 2019, the gas market reached a value of about € 15 billion.
- European PV market is forecast for double-digit yearly growth. It grew by >100 % in 2019.
- OLEDs for next-generation flexible displays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

Bureau International des Poids et Mesures
ISO
UNI UN MONDO FATTO BENE
BallWave
MECO INC
Air Liquide creative oxygen
SOL SOLGROUP
SCOR Scientific Committee on Oceanic Research
IAPWS
IAPSO The International Association for the Physical Sciences of the Oceans (IAPSO)
Baker Hughes
LI-COR
BOC A Member of The Linde Group
SAPIO GRUPPO
NMIJ
KRISS
rotronic MEASUREMENT SOLUTIONS
PST PROCESS SENSING TECHNOLOGIES
SIAD
Ha FUNDACIÓN PARA EL DESARROLLO DE LAS NUEVAS TECNOLOGÍAS DEL HIDRÓGENO EN ARAGÓN
semi
ACCREDIA L'ENTE ITALIANO DI ACCREDITAMENTO
EffecTech Global Leaders in Gas Measurement

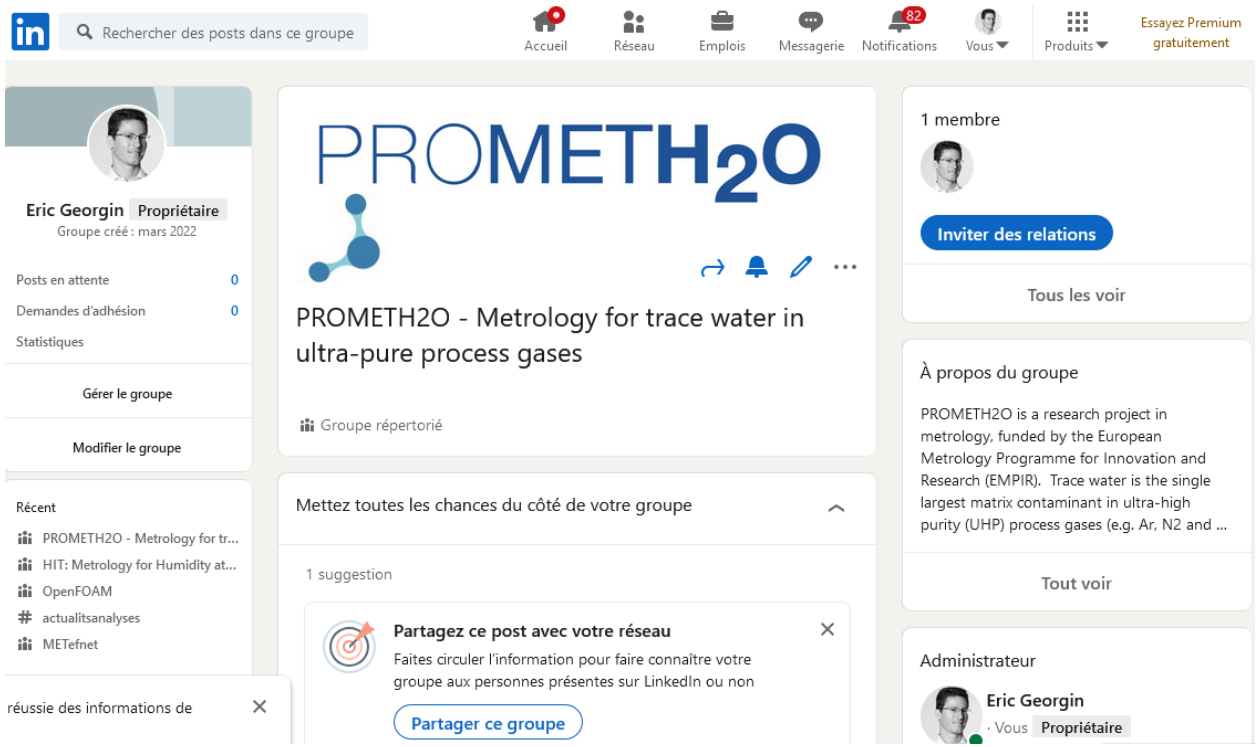
**21 organisations have joined the SB so far**

# In summary, PROMETH2O will …

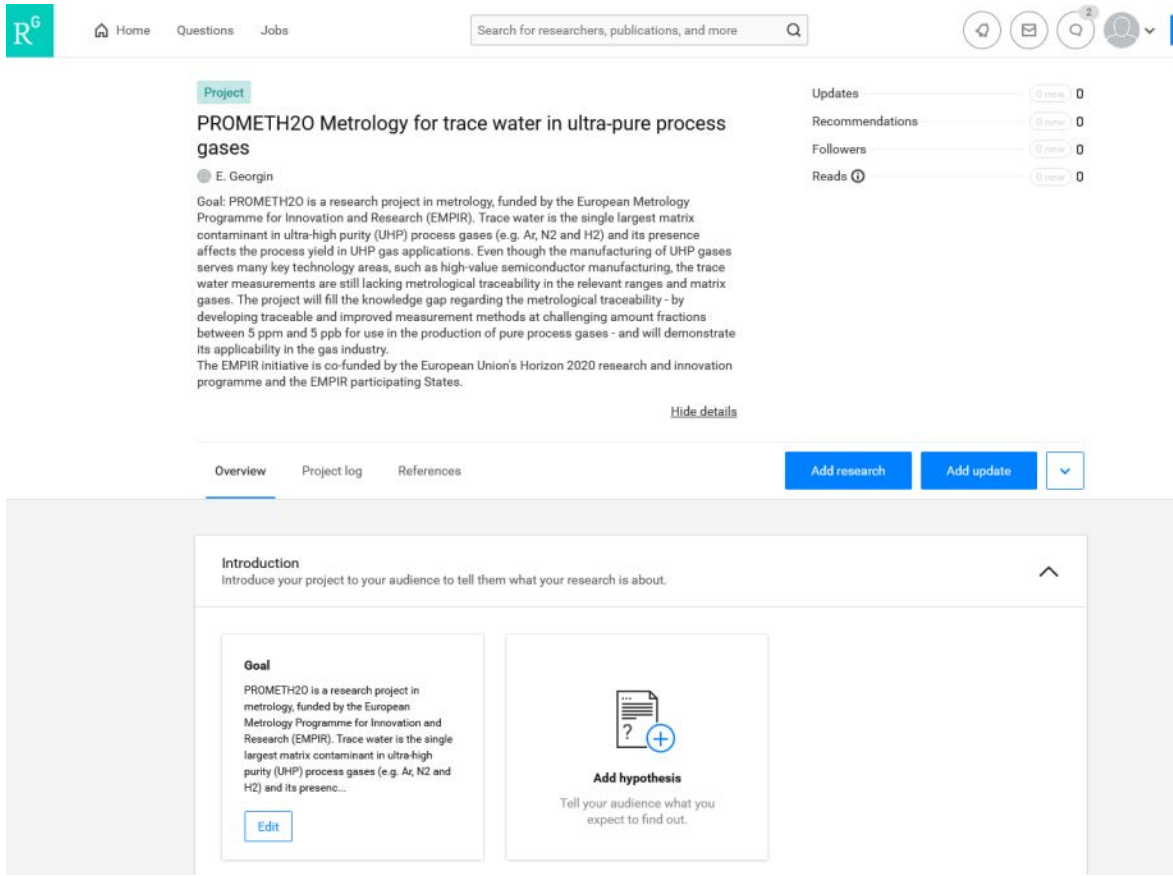
- Improve **trace water measurement** methods and techniques [in the range **from 5 nmol/mol to 5 μmol/mol**].
- Provide **robust traceability** to trace water measurements by developing suitable standards down **to 5 nmol/mol (-105 °C fp) in $N_2$, Ar and $H_2$**.
- Improve the knowledge of **thermophysical data** (w.v. enhancement factor) 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.

# Stay in touch

## LinkedIn




## Research gate



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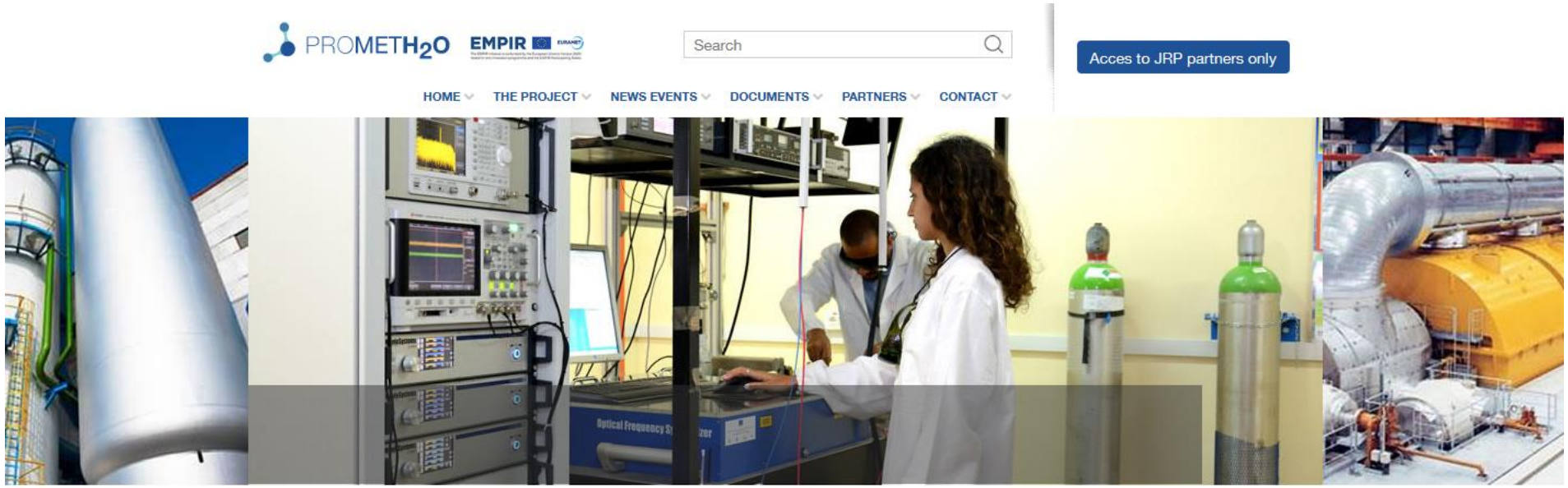


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*Thank you for your attention!*