PROMETH$_2$O

20IND06 PROMETH2O

Metrology for trace water in ultra-pure process gases

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Vito Fernicola, INRIM, Italy

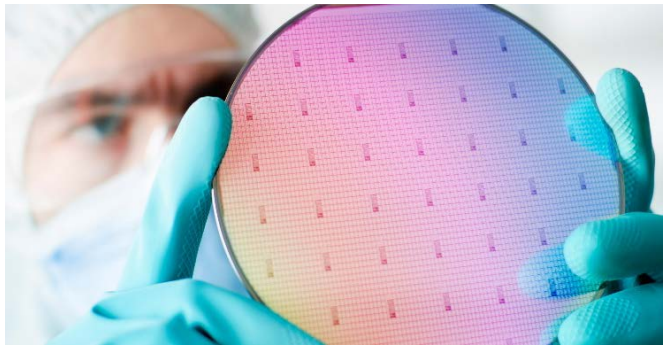
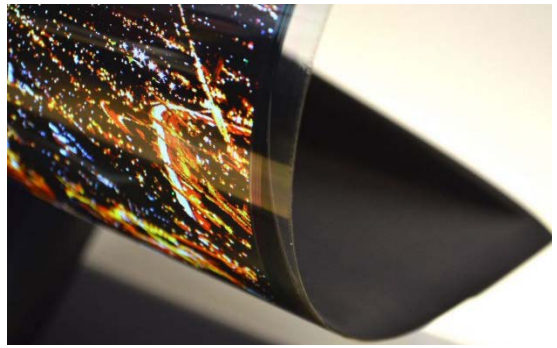
Workshop and Training @ Nippon Gases

Torino, 7th of March 2024

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).

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

Global market for industrial gas reached $95 billion in 2020. It grew at 5 % per year.

In Europe, in 2020, the gas market reached a value of about € 15 billion.

Needs for ultra-pure process gases

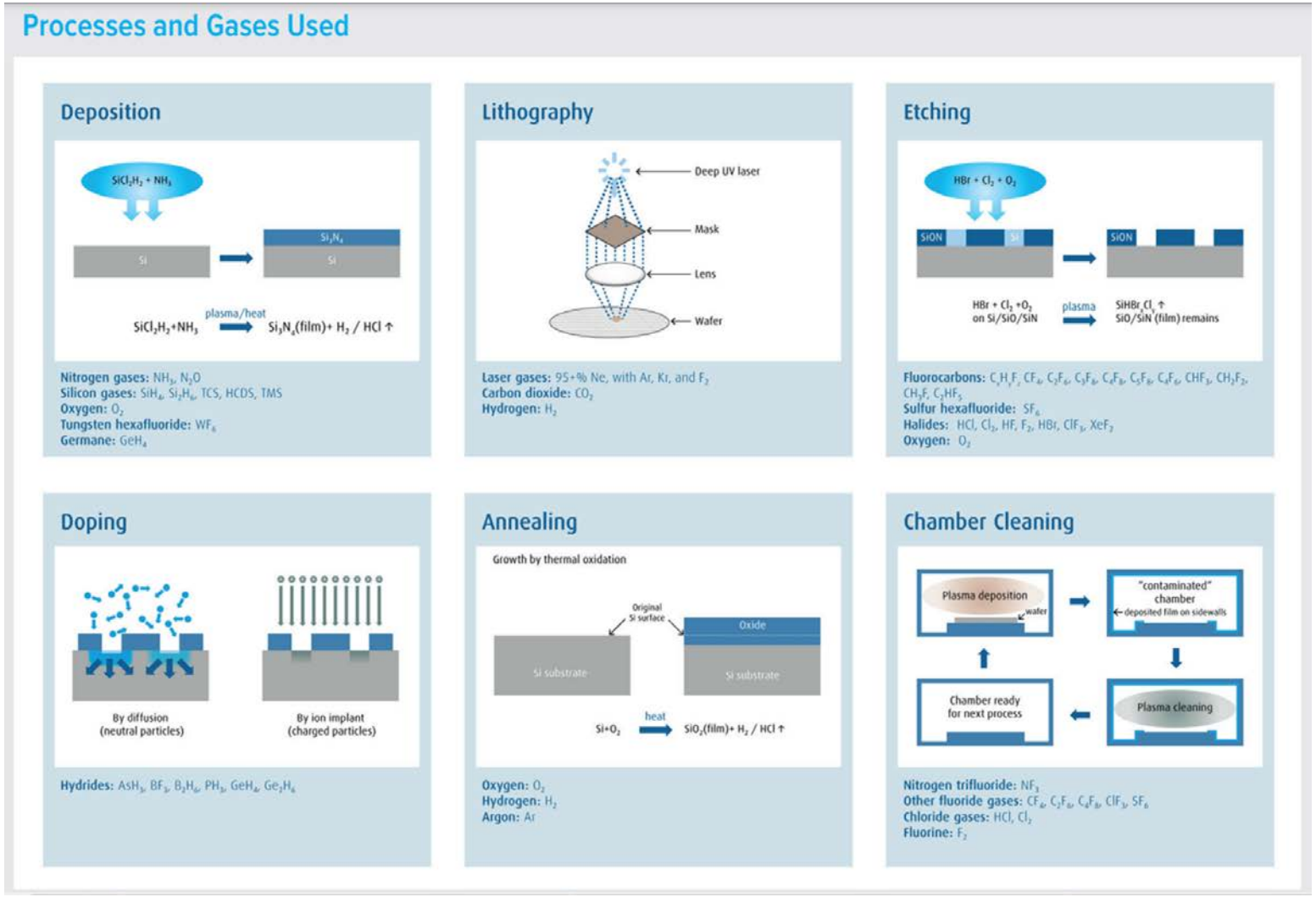
https://www.linde-gas.com/en/images/Gasworld%20-%20Creating%20a%20Semiconductor%20FEB18_tcm17-477345.pdf

gasworld • February 2018

gasworld.com/specialty-gas-zone

Creating a semiconductor and the gases that make it happen

By Dr. Paul Stockman, Head of Market Development, Linde Electronics



Project challenges

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

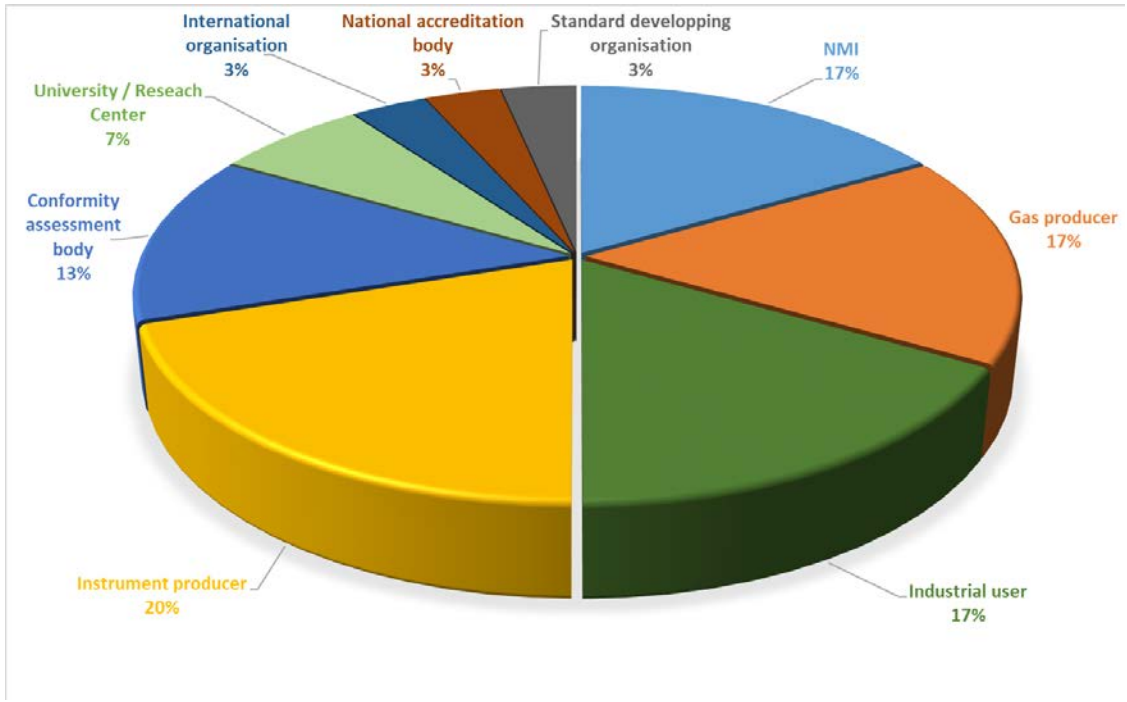
Its measurement presents **great challenges to both gas manufacturers and analytical instrument makers**.

The project is aiming at:

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

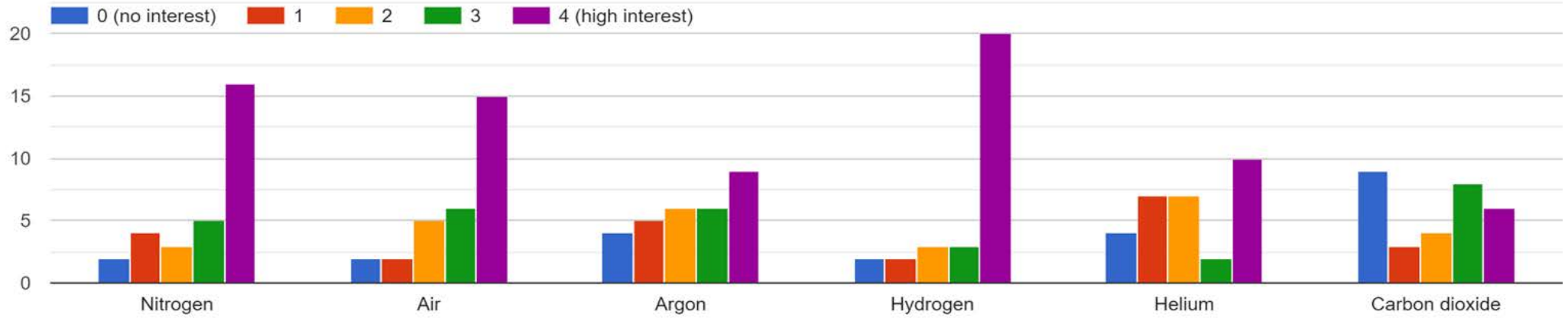
Stakeholder engagement

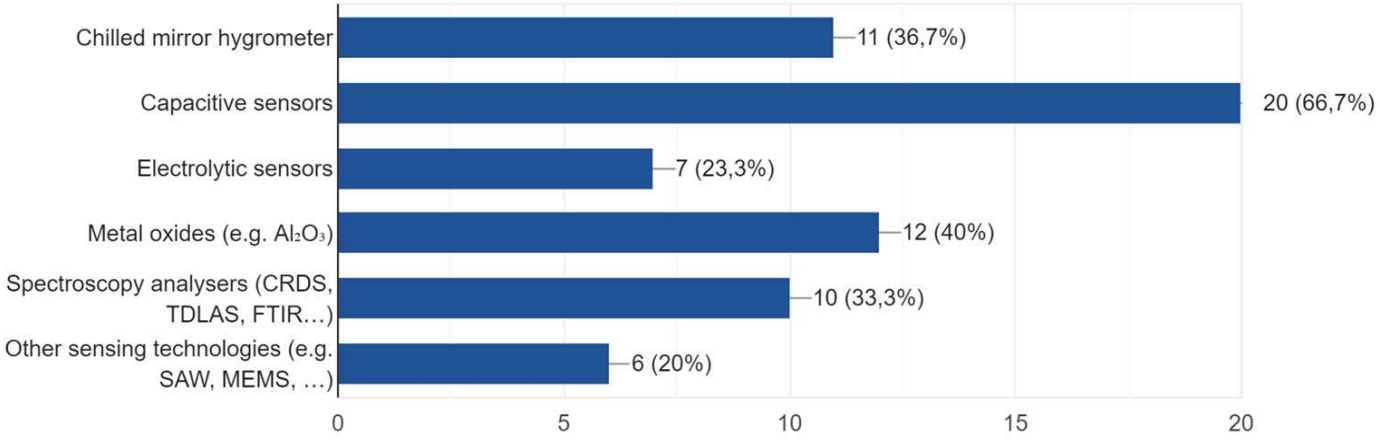
Surveying stakeholders needs and priorities



Steering Board made of 21 key stakeholders among gas producers, instrument manufacturers, and international scientific organisations.

Surveying stakeholder needs and priorities





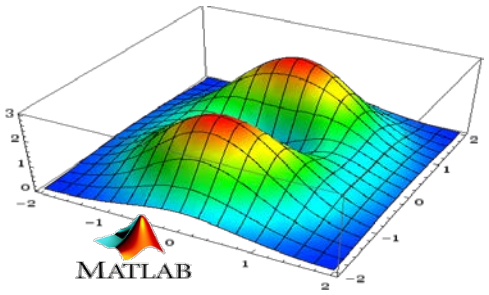
"I need to measure the trace water content in pure process gases as part of the quality assurance process."

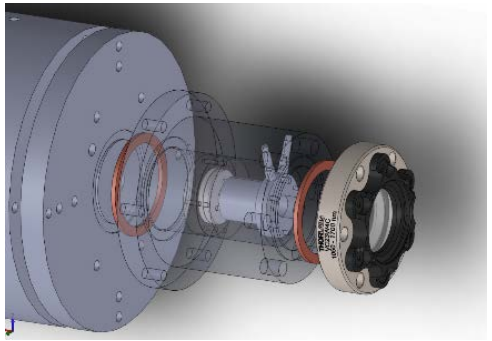
"We focus on hydrogen production by water electrolysis and fuel cell applications."

"We need an international traceable system for calibration at under 0.1 ppm."

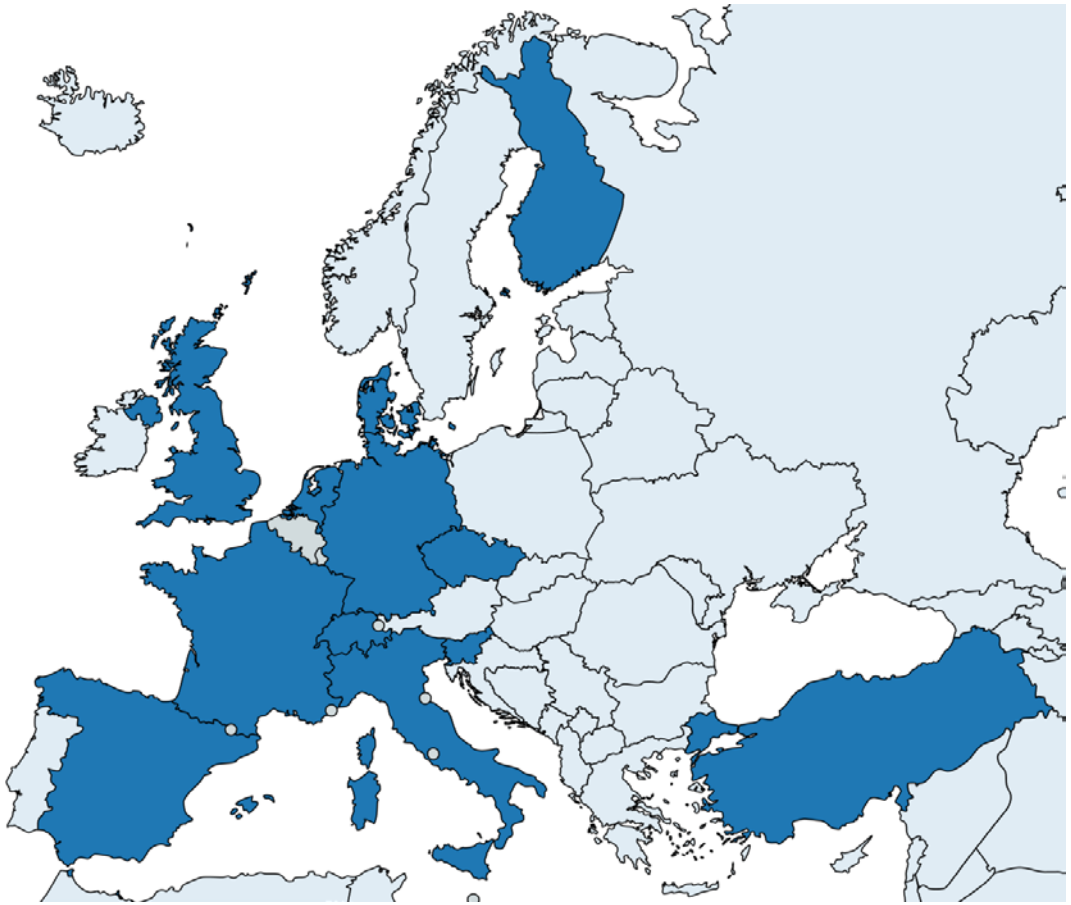
Project objectives

- **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/improved measurement methods** in the amount fraction range between 5 μmol/mol and 5 nmol/mol (*rel. uncertainty* 3 % to 8 %).
- **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 industrial facilities** with real-time measurements and on-site calibrations.
- **Toolkits of metrological solutions** for robust measurement traceability in the production of UHP process gases.





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

New primary standards for trace water measurements

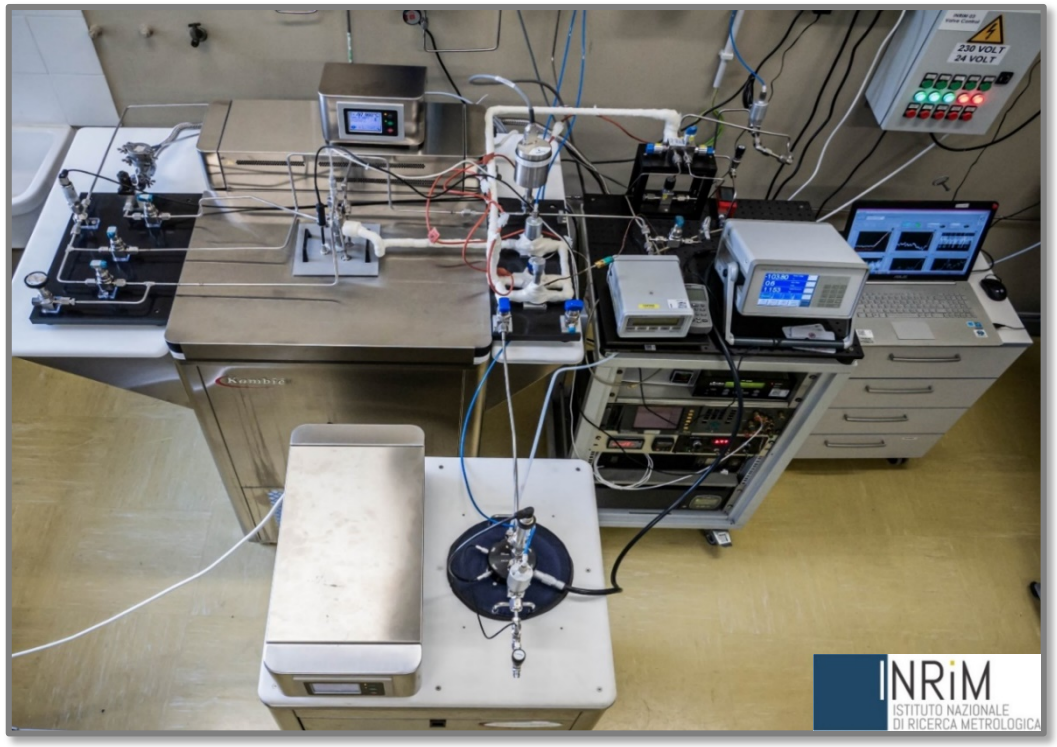
Development and improvement of primary humidity standards

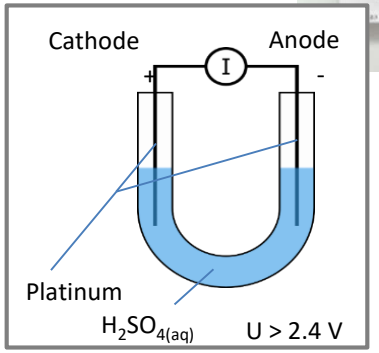
- Trace water in Ar and N_2 from 5 ppm down to 5 ppb (Rel. uncertainty: 3 % to 8 %)
- Frost point temperature from -65 °C down to -105 °C (Std. uncertainty: 0.35 °C at -105 °C)
- Operating pressure up to 1 MPa

6x systems

- ❑ Three thermodynamic saturation-based frost point generators;
- ❑ A Coulometric trace water generator;
- ❑ A permeation system based on a magnetic suspension balance;
- ❑ A dilution-based (two-flow) humidity generator.

Achievements: Primary standards for trace water





PTB
Physikalisch-Technische Bundesanstalt
Nationales Metrologieinstitut

LFP primary humidity generator - Mark 2

- ❑ Frost-point temperature: -105 °C to -20 °C
- ❑ Water vapour mole fraction: 5 ppb to 1000 ppm
- ❑ Pressure: 200 hPa to 0.68 MPa (N_2 and Ar)

Coulometric Trace Water Generator (CTWG)

- ❑ Amount fraction > 5 ppb
- ❑ Rel. uncertainty: 8 %

Permeation system based on a passivated MSB

- ❑ Range: 50 ppb to 5 ppm

Improved (trace water) measurement methods

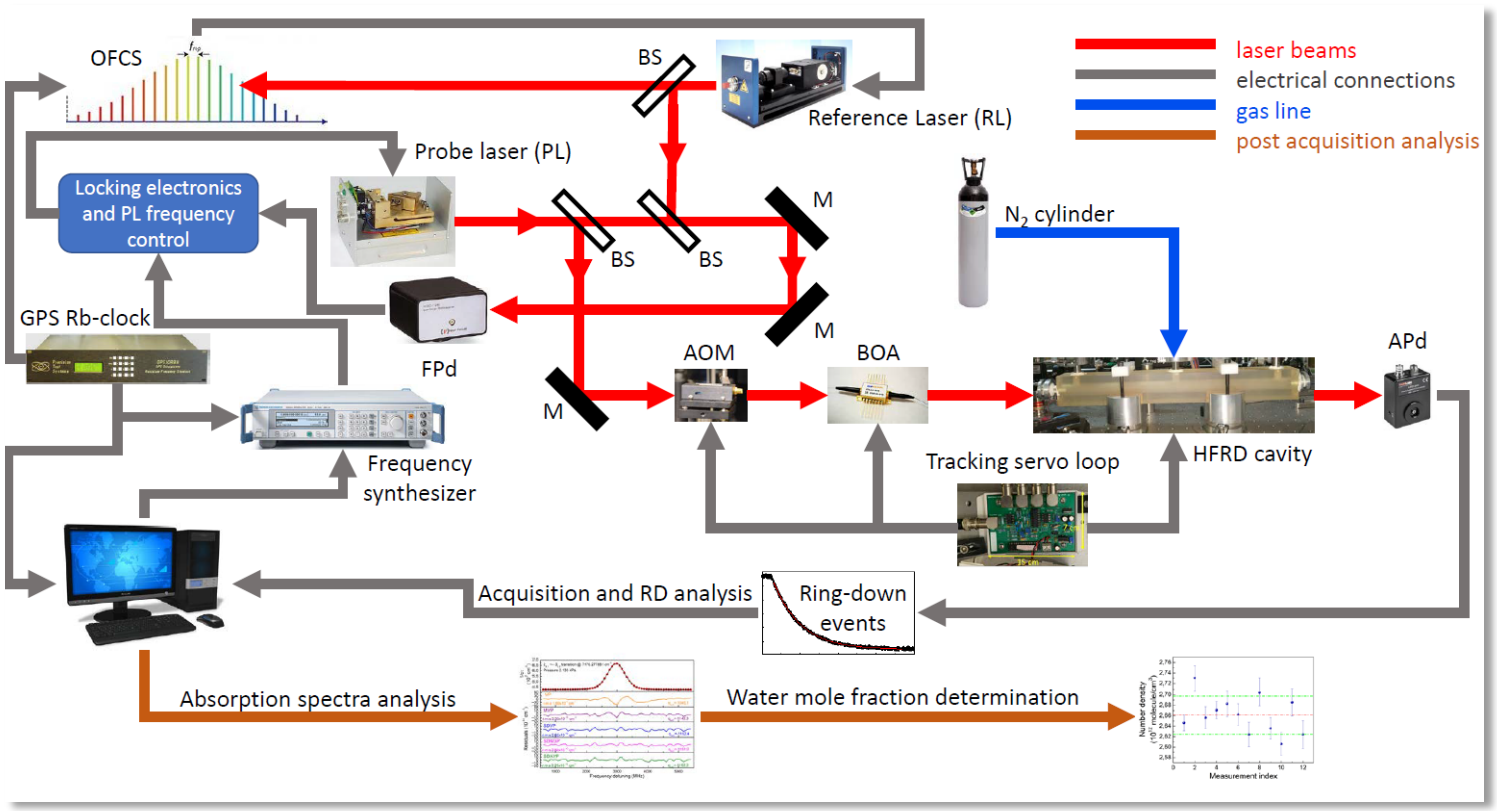
Development and improvement of optical analysers

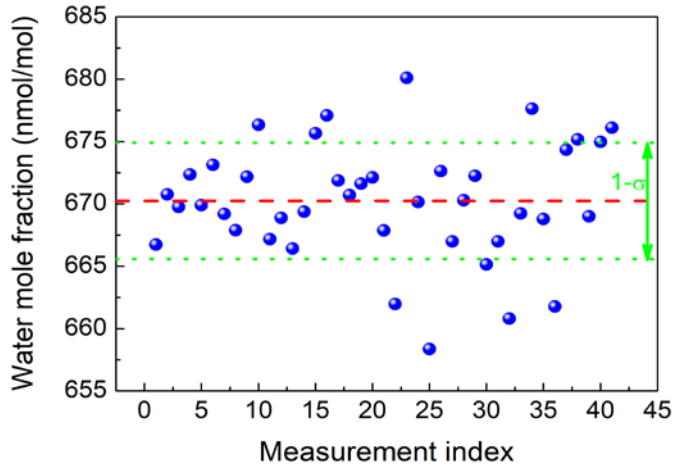
- Target: H_2O traces in Ar, N_2, H_2 [from 5 ppm (-65 °C) to 5 ppb (-105 °C) @ 0.1 MPa].
- Relative uncertainty: 3 % (at 5 ppm) to 8 % (at 5 ppb)

4x systems

- ❑ 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.

Achievements: Improved comb-assisted CRDS optical analyser



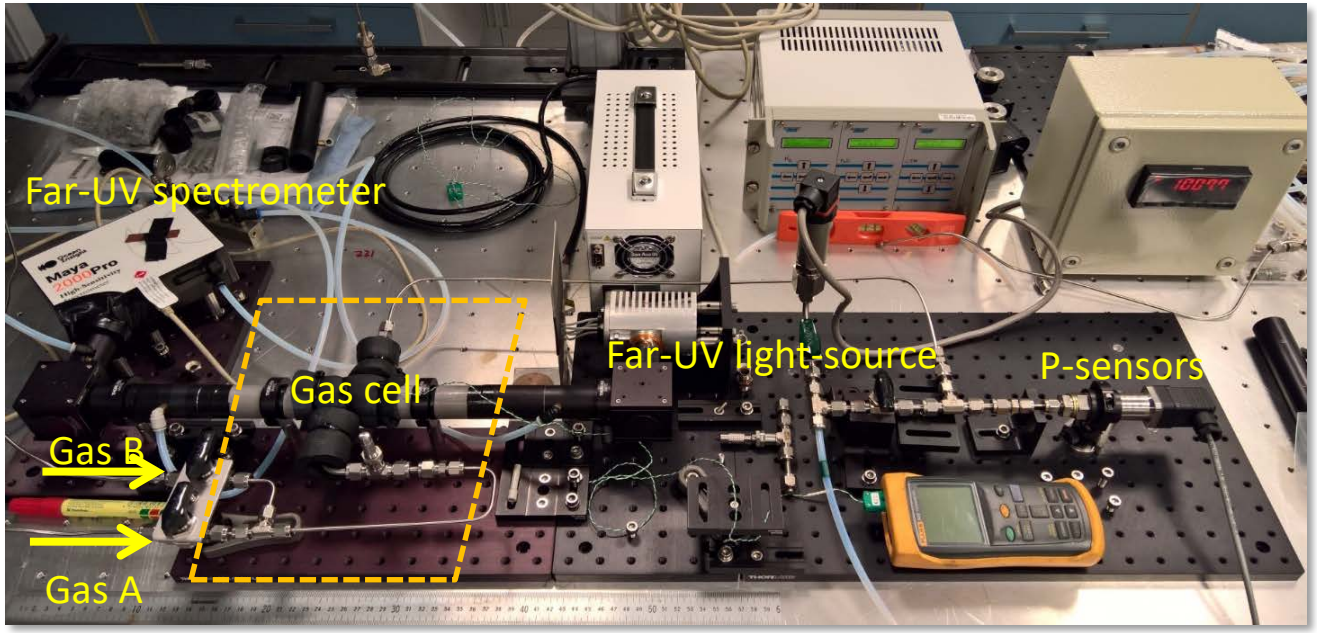


$$x_w = (671 \pm 4)\ nmol/mol$$

Contribution (k=1)	Type A (%)	Type B (%)
Statistical	**0.5**	
Line strength		**0.3**
Frequency scale		**Negl.**
Line shape model (SDVP)		**0.1**
RD per point & frequency step		**< 0.2**
Laser scan width		**< 0.2**
Gas temperature		**0.05**
Partition function		**0.04**
Pressure		**0.05**
Overall combined uncertainty = 0.7 %		

Università degli Studi della Campania *Luigi Vanvitelli*

Achievements: Improved trace water analysers and Enhancement factor measurements

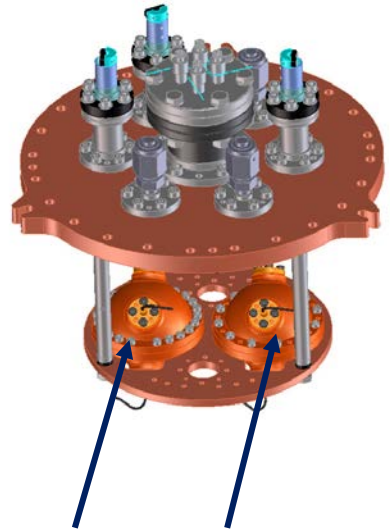


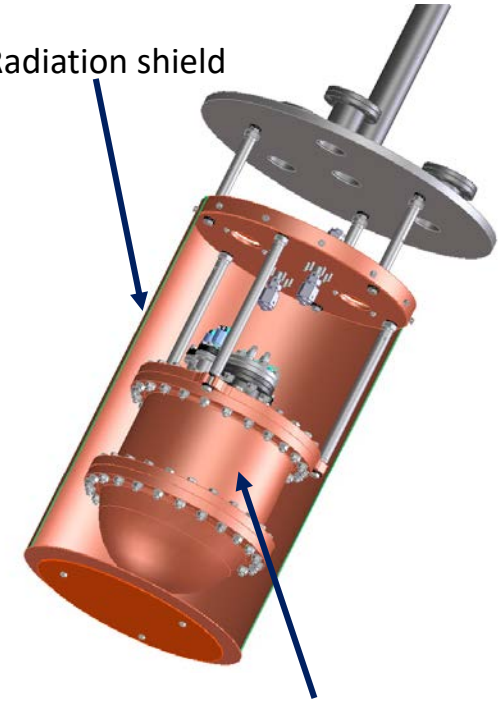
Far-UV spectroscopy system

- highly-modular gas cells: (0.5 to 100) cm;
- flow or static measurement: (0 to 100) bar;
- 100-cm cell with DURSAN® coatings;
- two-way spectra analysis: “full” and “DOAS”

Microwave-based trace water hygrometers

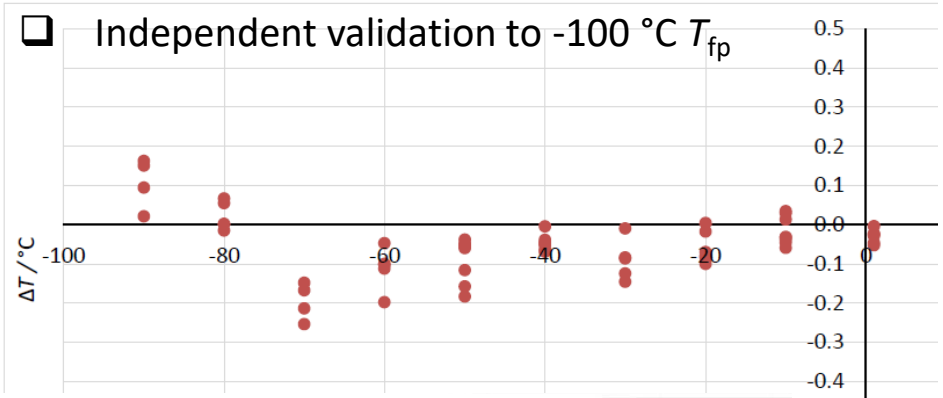
to measure the enhancement factor of H_2O vapour in N_2, Ar, and H_2





Achievements: Provision of (on-site) traceability

Accelerated development and validation of a portable frost point generator (FPG)



VAISALA

Qrometric
Industrial and scientific metrology

MBW calibration

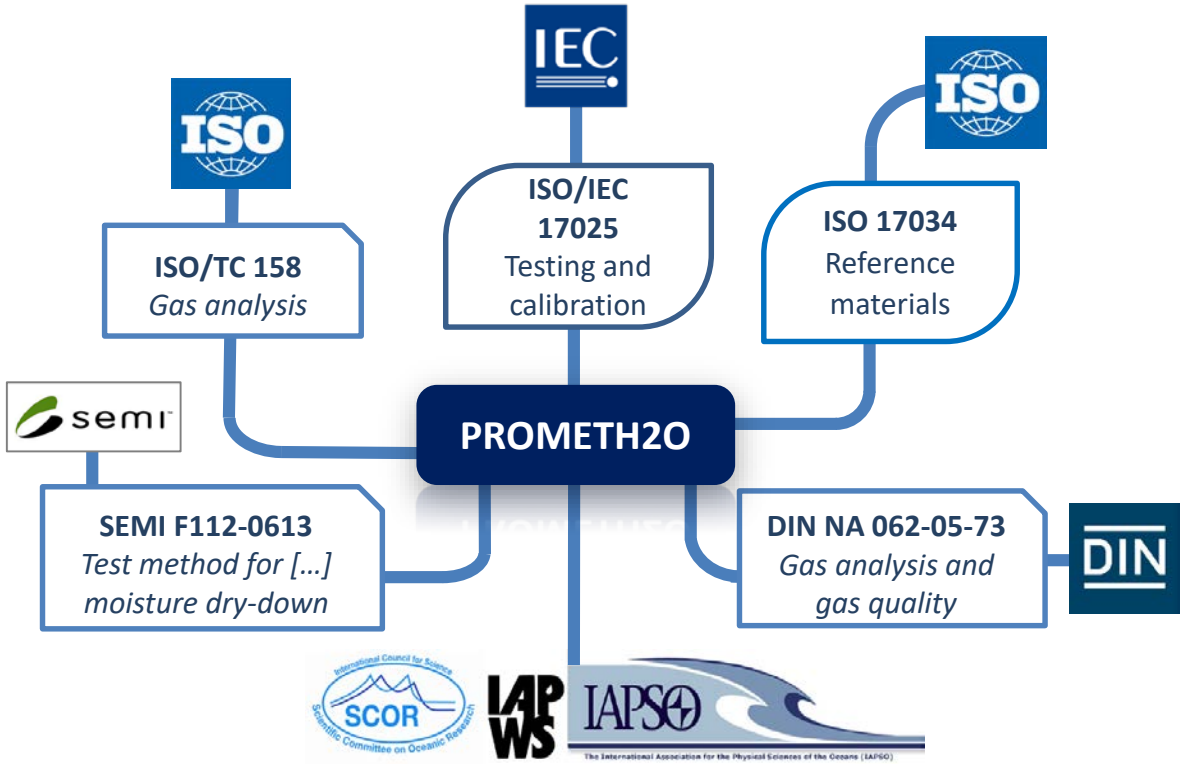
Traceable assessment of state-of-the-art commercial hygrometers
down to -105 °C (5 ppb)

NIPPON GASES

Test bed demonstrators
Industrial production facility of speciality gases that includes pure and UHP gases and humid gas mixtures.

Making an impact …

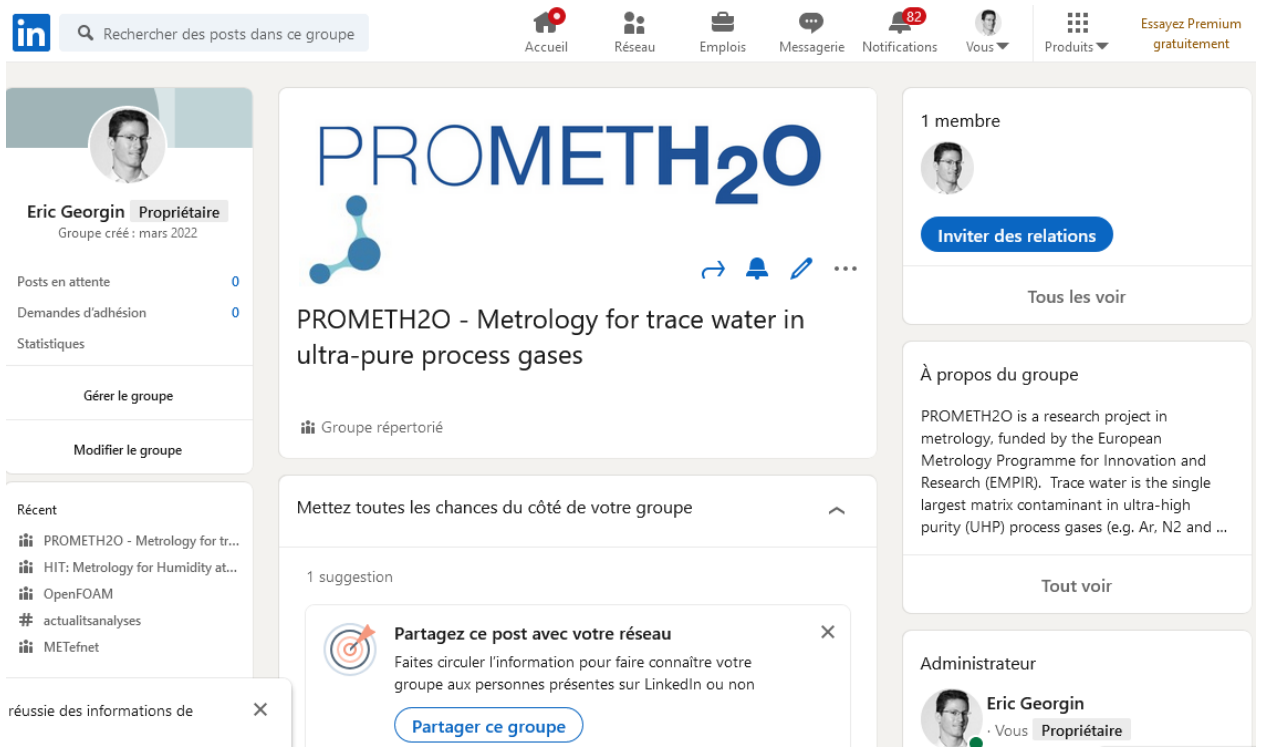
- Availability of **primary standards** and **transfer standards** to provide traceability, also via calibration services, to trace water analysers.
- **Measurement range:** 5 μmol/mol to 5 nmol/mol, or equivalently -65 °C to -105 °C frost point.
- **Documented and validated software tools** to estimate the enhancement of water vapour in N_2 and Ar and its uncertainty in the range between -30 °C and -90 °C and pressure up to 1 MPa.
- **Early impact on UHP gas manufacturing**: on-site traceable calibration of water contamination at industrially-relevant facilities.



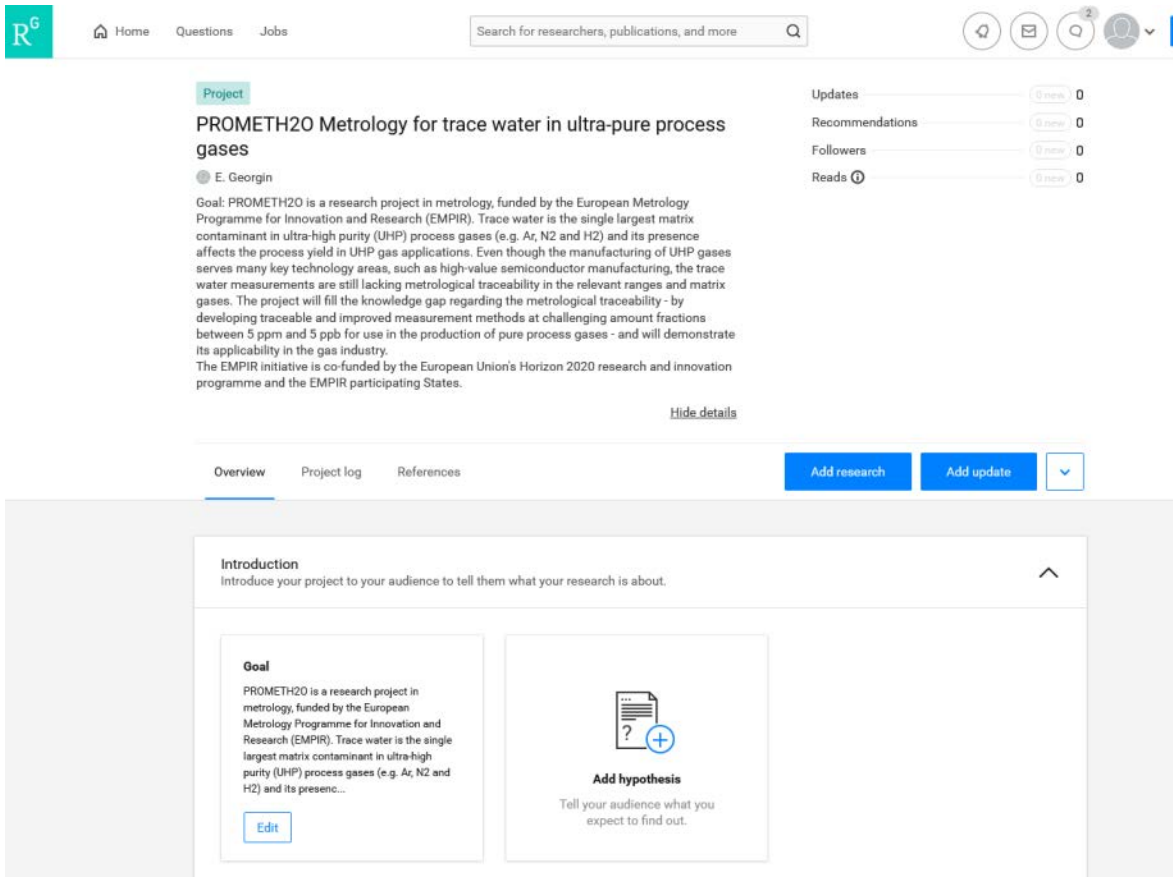
- **Establishment of an European-wide measurement infrastructure.**

Stay in touch

LinkedIn



Research gate



Stay in touch

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