PROMETH2O

Measurement challenges for trace water in pure gases

Stephanie Bell, National Physical Laboratory, UK

20IND06 PROMETH2O - Final Workshop
Gas Analysis 2024 / Porte de Versailles, Paris - France
Tuesday 30th of January 2024

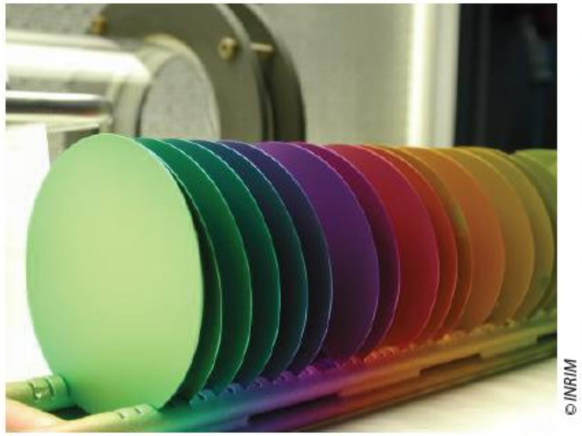
EMPIR EURAMET
The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Measurement challenges - Contents

I will say something about:

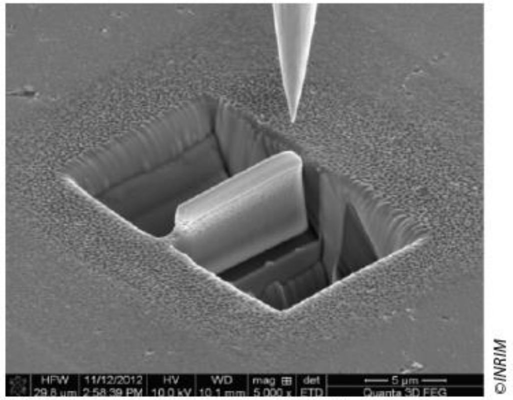
- The drivers - applications, and use of multiple gases
- Humidity metrology
- Challenges
  - of the trace range
  - of multiple measurement principles
  - of multiple gases and gas non-ideality
- Conclusions

Needs for ultra-pure process gases



LPCVD process of silicon wafers

OLED products



MEMS device fabrication and manipulation

Solar photovoltaic (PV) panels

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

gasworld • February 2018

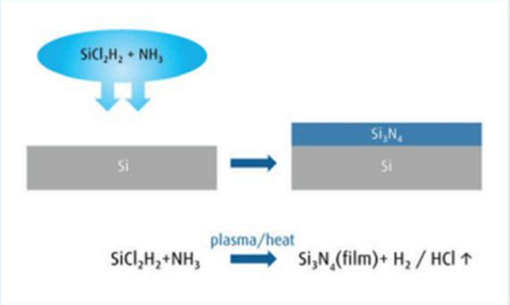
gasworld.com/specialty-gas-zone

Creating a semiconductor and the gases that make it happen

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

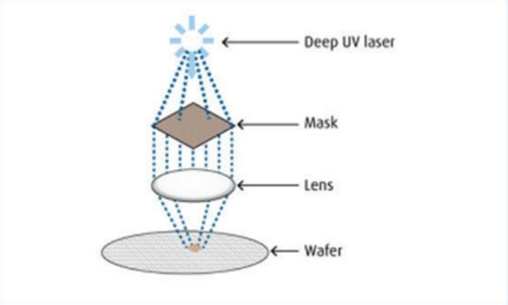
Processes and Gases Used

Deposition



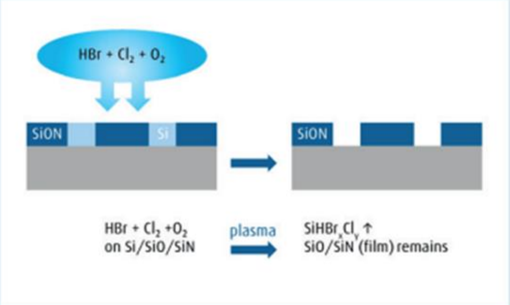
Nitrogen gases: NH_3, N_2O
Silicon gases: SiH_4, Si_2H_6, TCS, HCDS, TMS
Oxygen: O_2
Tungsten hexafluoride: WF_6
Germane: GeH_4

Lithography



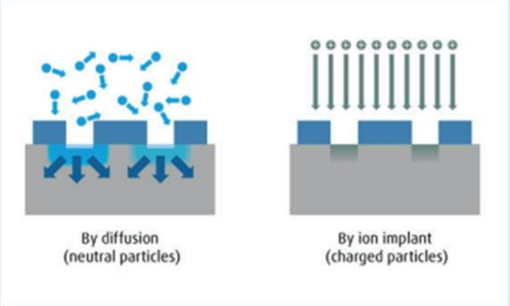
Laser gases: 95+% Ne, with Ar, Kr, and F_2
Carbon dioxide: CO_2
Hydrogen: H_2

Etching



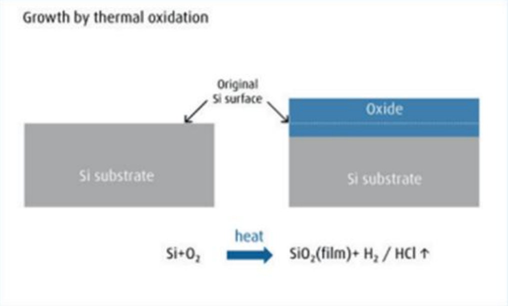
Fluorocarbons: $C_xH_yF_z$, CF_4, C_2F_6, C_3F_8, C_4F_8, C_5F_8, C_4F_6, CHF_3, CH_2F_2, CH_3F, C_2HF_5
Sulfur hexafluoride: SF_6
Halides: HCl, Cl_2, HF, F_2, HBr, ClF_3, XeF_2
Oxygen: O_2

Doping



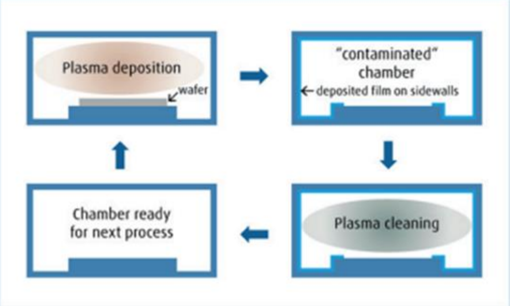
Hydrides: AsH_3, BF_3, B_2H_6, PH_3, GeH_4, Ge_2H_6

Annealing



Oxygen: O_2
Hydrogen: H_2
Argon: Ar

Chamber Cleaning



Nitrogen trifluoride: NF_3
Other fluoride gases: CF_4, C_2F_6, C_4F_8, ClF_3, SF_6
Chloride gases: HCl, Cl_2
Fluorine: F_2

PRO MET H_2O

...gases

https://www.nist.gov/pml/ser... science/fluid-metrology/datab... thermophysical-properties-gas... used-semiconductor-0

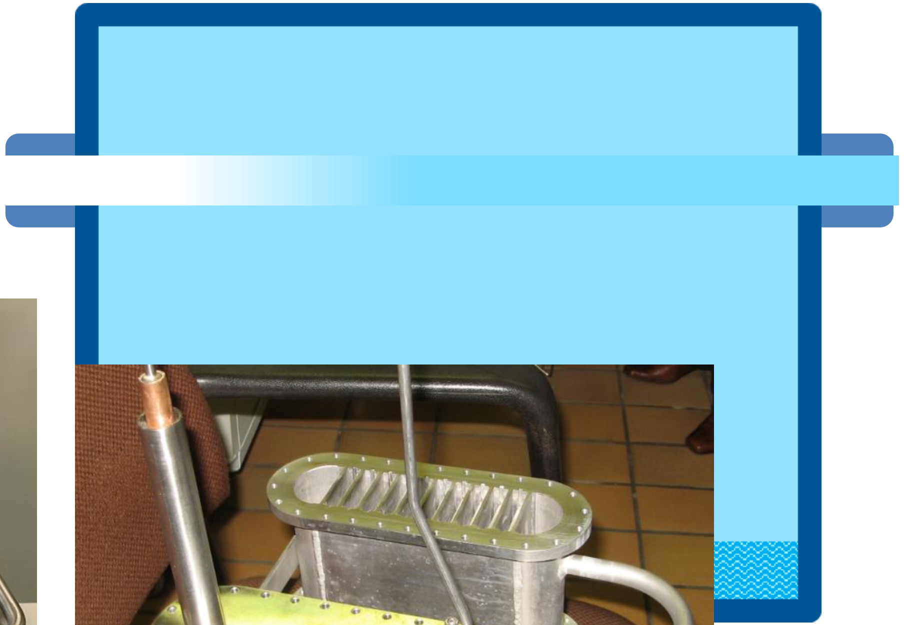
Ammonia	NH_3	Nitrous Oxide	N_2O
Argon	Ar	Nitrogen Trifluoride	NF_3
Allene	C_3H_4	Nitrogen	N_2
Arsenic Trifluoride	AsF_3	Oxygen	O_2
Arsine	AsH_3	Phosgene	$COCl_2$
Trimethyl Arsine	$As(CH_3)_3$	Phosphourous Trifluoride	PF_3
Diborane	B_2H_6	Phosphorous Pentafluoride	PF_5
Pentaborane	B_5H_9	Phosphine	PH_3
Boron Trichloride	BCl_3	Sulfur Dioxide	SO_2
Bromine	Br_2	Stibine	SbH_3
Carbon Dioxide	CO_2	Silane	SiH_4
Carbon Monoxide	CO	Disilane	Si_2H_6
Carbon Tetrafluoride	CF_4	Silicon Tetrachloride	$SiCl_4$
Chlorine	Cl_2	Silicon Tetrafluoride	SiF_4
Chlorine Trifluoride	ClF_3	Sulfur Hexafluoride	SF_6
Ethylene Oxide	C_2H_4O	Titanium Tetrachloride	$TiCl_4$
Helium	He	Tungsten Hexafluoride	WF_6
Hexafluoroethane	C_2F_6	Uranium Hexafluoride	UF_6
Hydrogen	H_2	Vinyl Bromide	C_2H_3Br
Hydrogen Bromide	HBr	Vinyl Fluoride	C_2H_3F

Need for metrology

- Water vapour is not listed as a process gas, but it is always present.
- Water vapour is challenging because it is
  … everywhere … reactive … polar (sticky).
- **Reduction** of water vapour and its effects
  ↳ *needs* **control**
  ↳ *needs* **measurement**
  ↳ *needs* **calibration**
  ↳ *needs* **metrological traceability.**

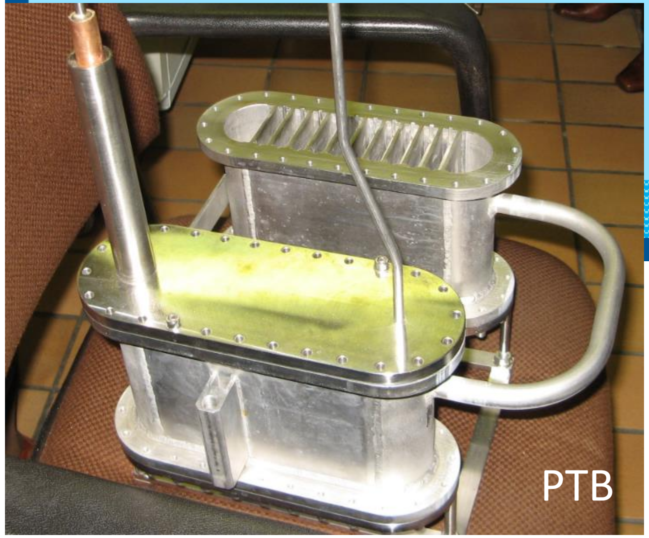
What we measure - humidity quantities in the SI

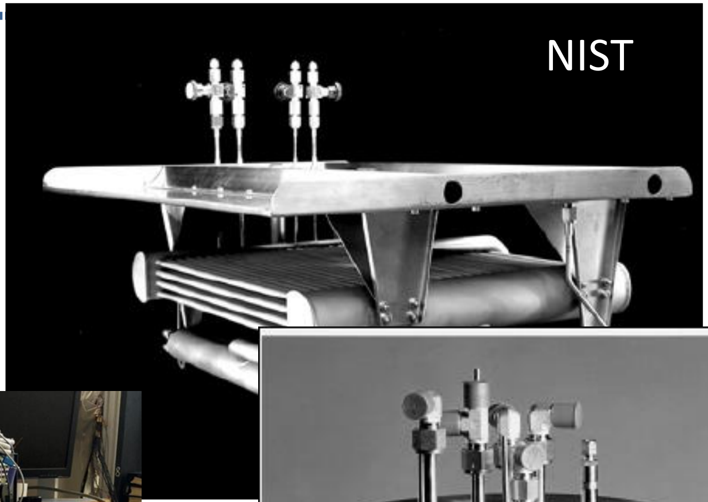
Phase equilibrium



Dry gas in →
(or preconditioned gas)

→
Humid gas out





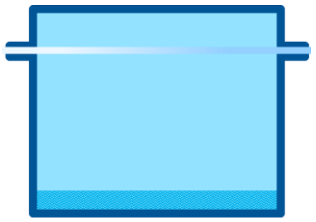
Realisation of saturation at defined temperature looks like this
In practice, dynamic equilibrium (efficient, with some uncertainty)

Humidity scales

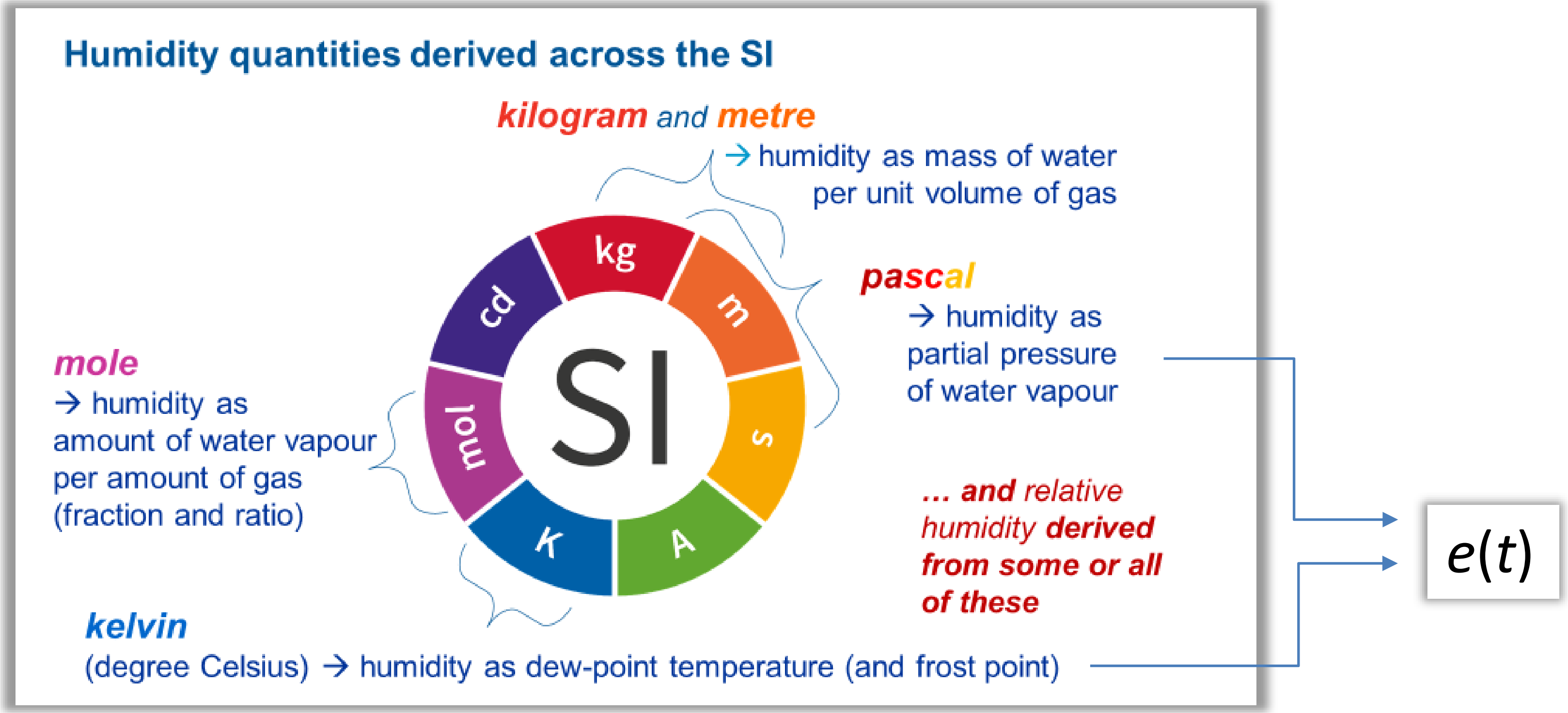
Generally, SI units are subdivided or multiplied to make a scale.

For humidity quantities, generally, at defined *T* and *P* …

- From saturation temperature
  - dew-point scale (dew point and frost point)
  - so-called "single-pressure generator"
- From saturation (at suitable over-pressure):
  - partial pressure is "subdivided" by expansion
  - "two-pressure generator"
- From saturation at any pressure:
  - concentration (however expressed) is "subdivided" by dilution with dry gas
  - "flow-mixing generator"
- And others, such as diffusion or permeation of water vapour (mass per unit time …)



Saturated gas
$z_{sat}(P,T)$



… and calculations to convert between quantities, often via vapour pressure of (pure) water, $e(t)$

Main challenges - overview

Some main challenges:

- Challenge of the trace range
  - Need for dry process gas
  - Calibration - reference dry gases – trace ranges
  - Impact of stray water
- Challenges of the use of multiple gases
  - Challenge of multiple measurement principles in this range and their sensitivity to different issues (pressure, species, response time, drift)
  - Challenge of gas non-ideality – water vapour enhancement factors

Challenge of the trace moisture range

- Need for dry process gas – to avoid product defects
- Example range 5 µmol mol^{-1} to 5 nmol mol^{-1} 5 ppm to 5 ppb
  (frost point at atmospheric pressure, -65 °C to -105 °C)
- Requires drying of process gas, and monitoring of this
- Stray water comes from desorption, leaks, back-diffusion (and residual trace water in gas as supplied)
- May be addressed by process flushing, baking, vacuum …
- Conditioning takes time

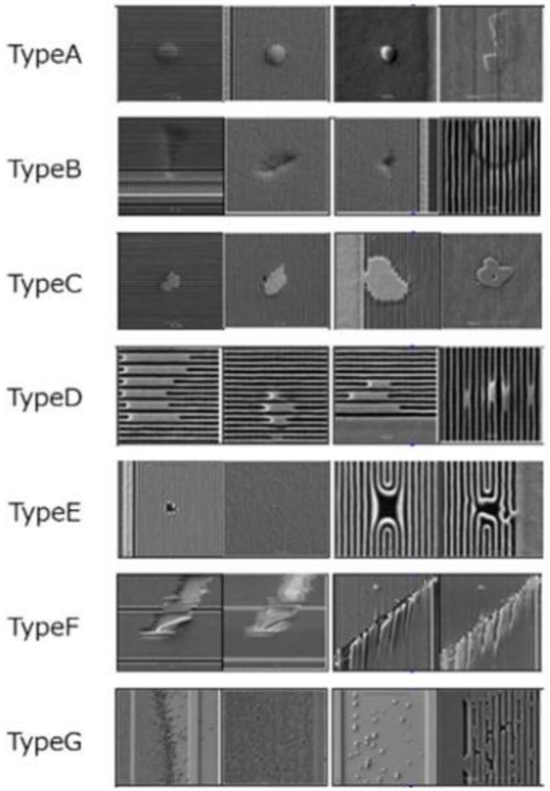


Fig. 1. Example of Defects.

Imoto et al., A CNN-Based Transfer Learning Method for Defect Classification in Semiconductor Manufacturing IEEE TRANSACTIONS ON SEMICONDUCTOR MANUFACTURING, VOL. 32, NO. 4, NOVEMBER 2019

Challenge of the trace moisture range

- Calibration in trace range - needs standards of accurate defined water content
  - mainly dynamically generated

- Saturation to defined frost point requires low saturation temperatures
  - Refrigeration challenges
- Two-pressure generation - less cooling, and pressure drop for speed
  - But requires formulae for vapour pressure and water vapour enhancement factor
- Flow mixing, blending, addition
  - (but zero gas …)

Stray water in calibration (again: desorption, leaks, back-diffusion …)

- We might not use vacuum, baking? We flush with dry gas and wait …
- Consequence is long wait times

Main challenges - overview

Some main challenges:

- Challenge of the trace range
  - Need for dry process gas
  - Calibration - reference dry gases – trace ranges
  - Impact of stray water
- Challenges of the use of multiple gases
  - Challenge of multiple measurement principles in this range and their sensitivity to different issues (pressure, species, response time, drift)
  - Challenge of gas non-ideality – water vapour enhancement factors

PRO MET H_2O

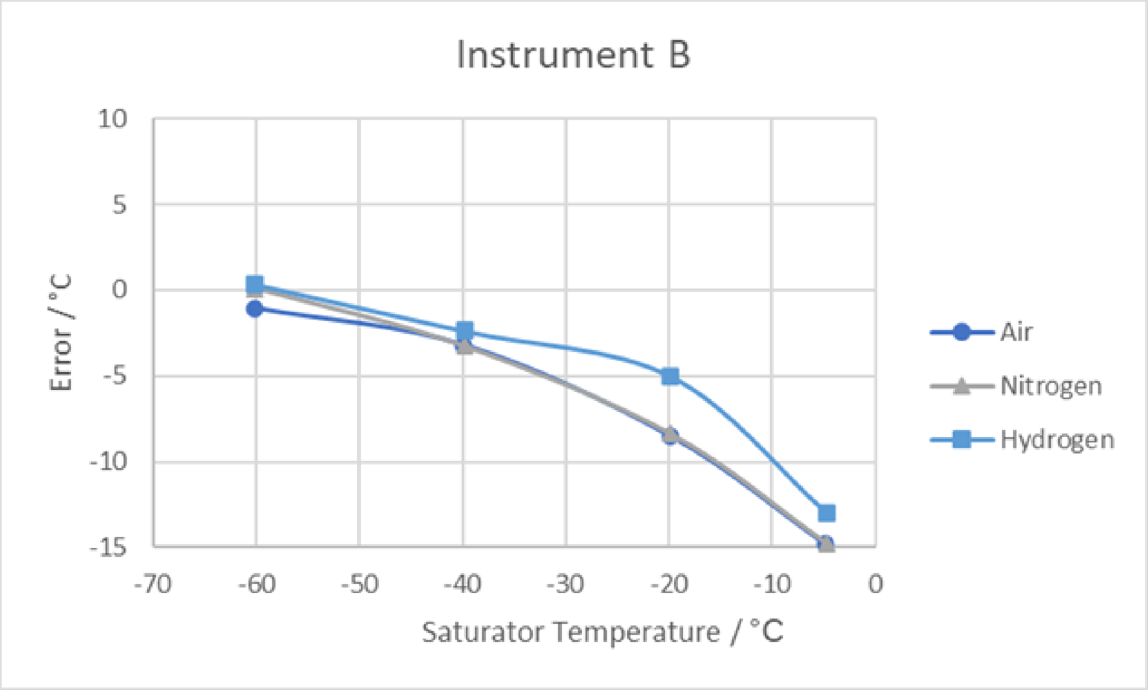
Sensing water vapour

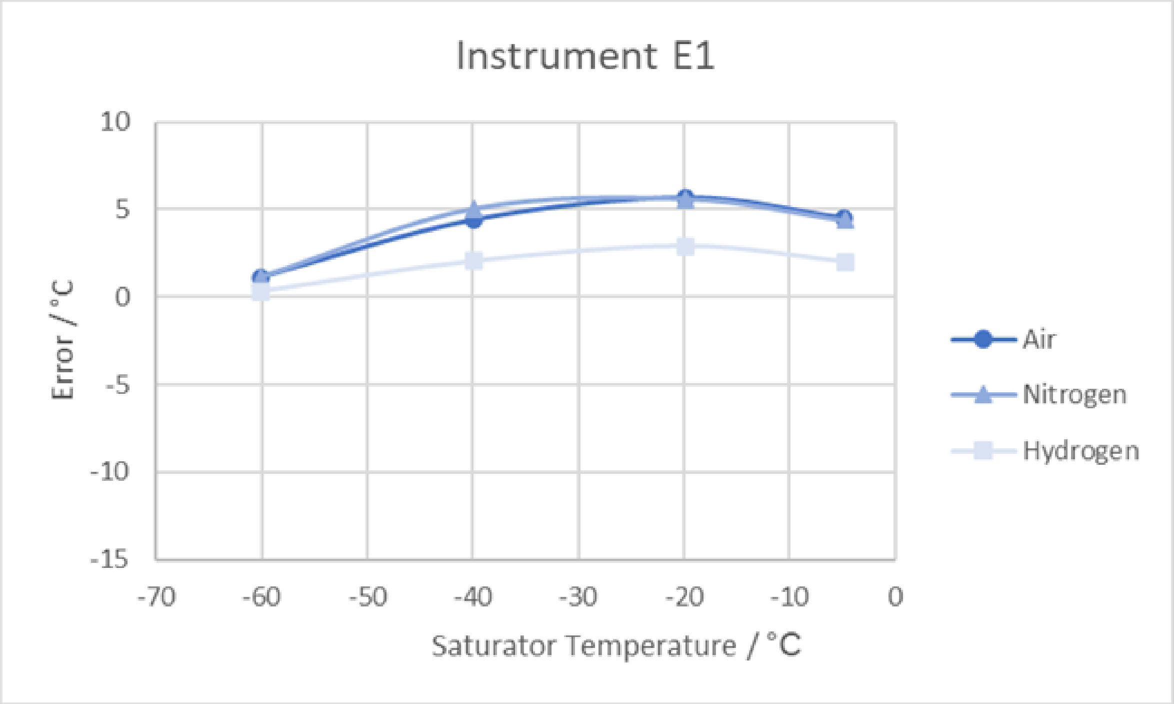
Principles include:

Electrical capacitance or resistance of sorbent film;
condensation (optical, SAW …);
spectroscopic (absorption or cavity ring-down);
electrolysis (P_2O_5); quartz oscillator; acoustic;
mass spec (APIMS); optical fibre; zirconia;
UV absorption/emission (Lyman-α); gravimetric;
evaporative cooling (psychrometer or wet- and dry-bulb hygrometer);
mechanical (dimensional change of “hair” or other);
LiCl conductance; colour change; adiabatic expansion (cloud chamber)

and others still emerging …

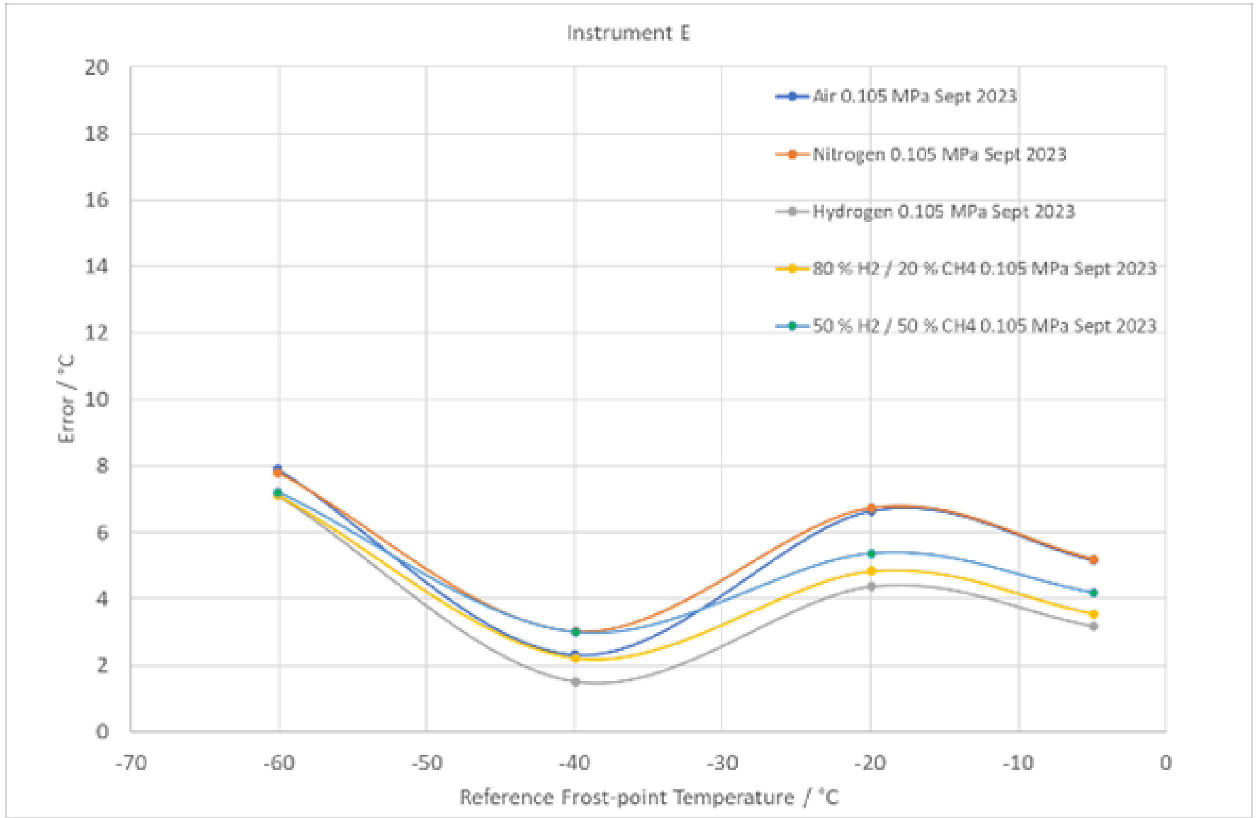
Graphs of sensing principles versus gas (mid to low range)



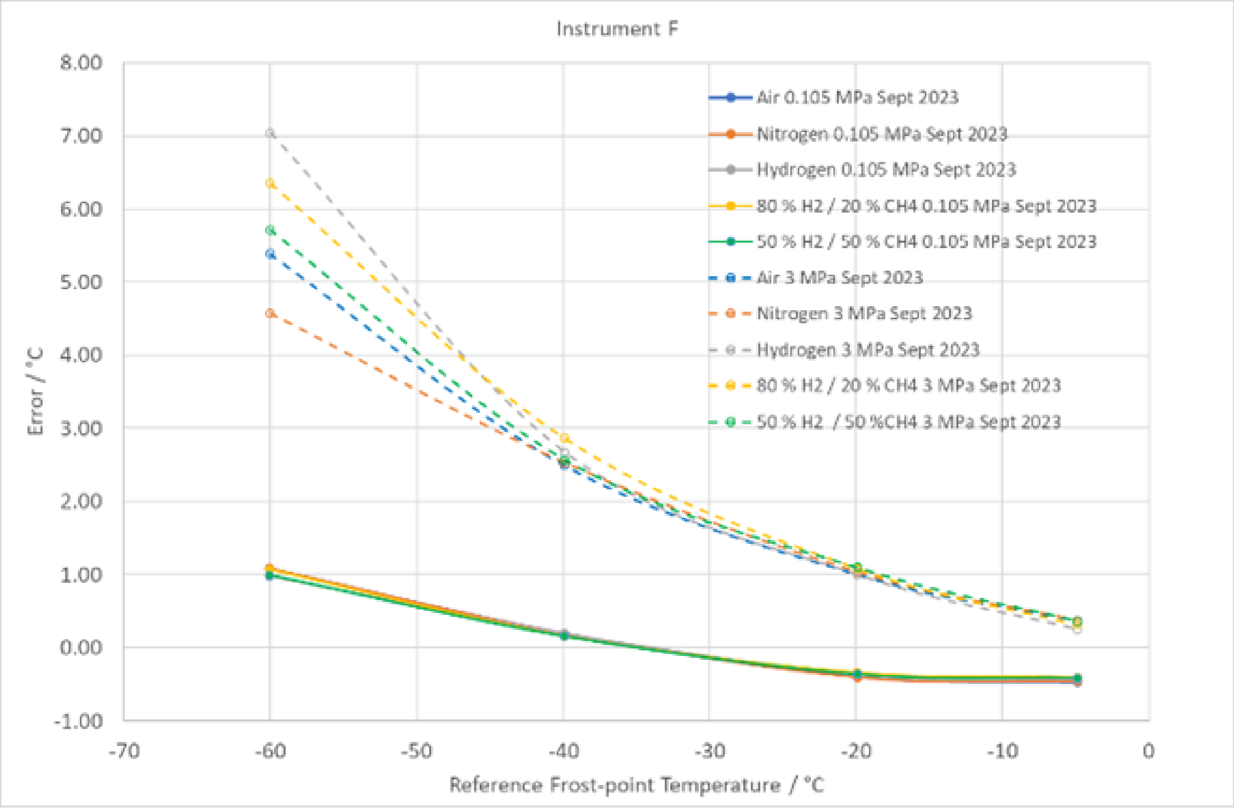


Instrument sensitivities

Hygrometer sensing principles – gas-dependence and pressure dependence



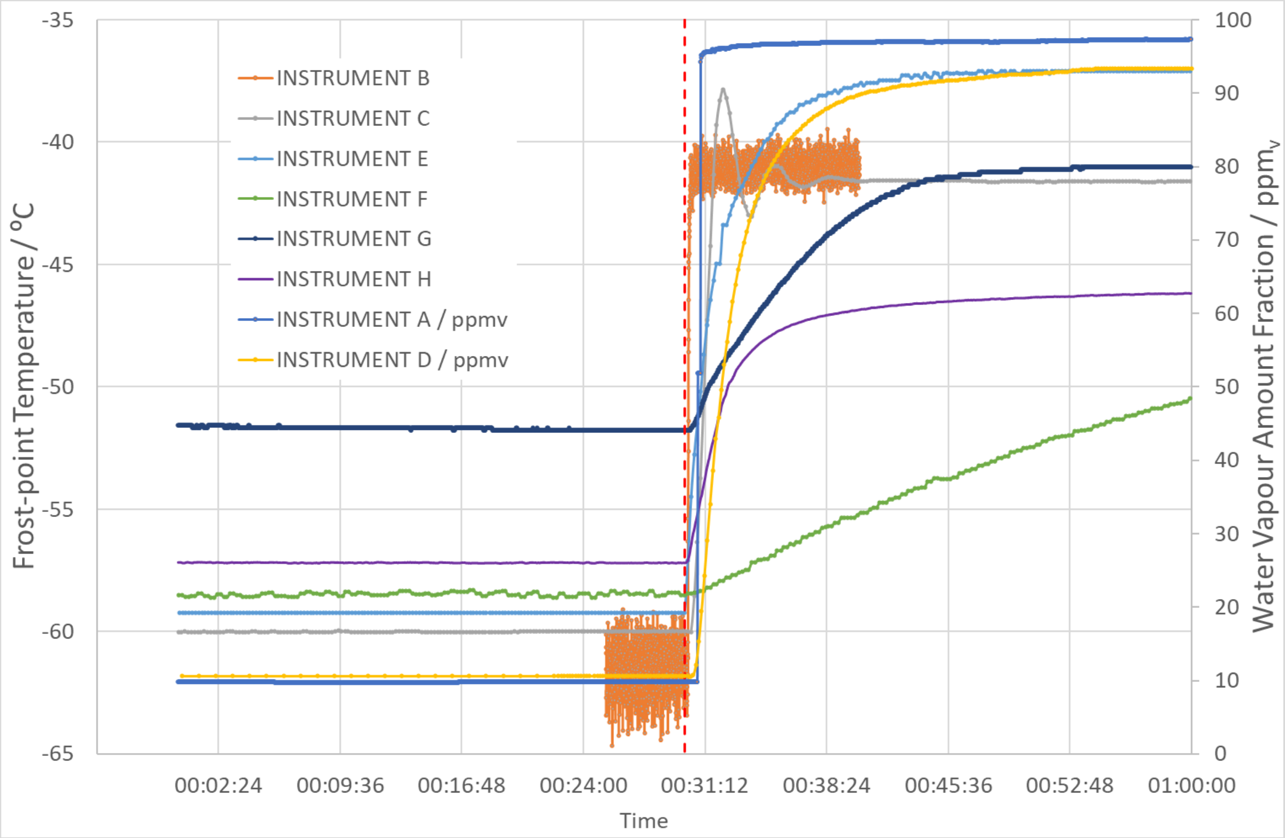
Near atmospheric pressure



Near atmospheric pressure and at 3 MPa

Instrument response times

Response time of a selection of instruments
step upwards from nominal 10 µmol mol^{-1} (frost point -60 °C)



Instrument	t_{90} response time / s
INSTRUMENT A	19.30
INSTRUMENT B	2.14
INSTRUMENT C	26.83
INSTRUMENT D	164.84
INSTRUMENT E	306.13
INSTRUMENT F	6872.48
INSTRUMENT G	786.62
INSTRUMENT H	402.72

t_{90} for INSTRUMENT F = 115 minutes

BUT ultra-trace range
→ nanomoles per mole (parts in 10 ^{9})
… far more challenging, much slower

Also, downwards response, hysteresis …

Challenge - multiple gases

- Challenges of the use of multiple gases
  - Challenge of multiple measurement principles in this range and their sensitivity to different issues (pressure, species, response time,
  - Challenge of gas non-ideality – water vapour enhancement factors, $f(P, t_d)$

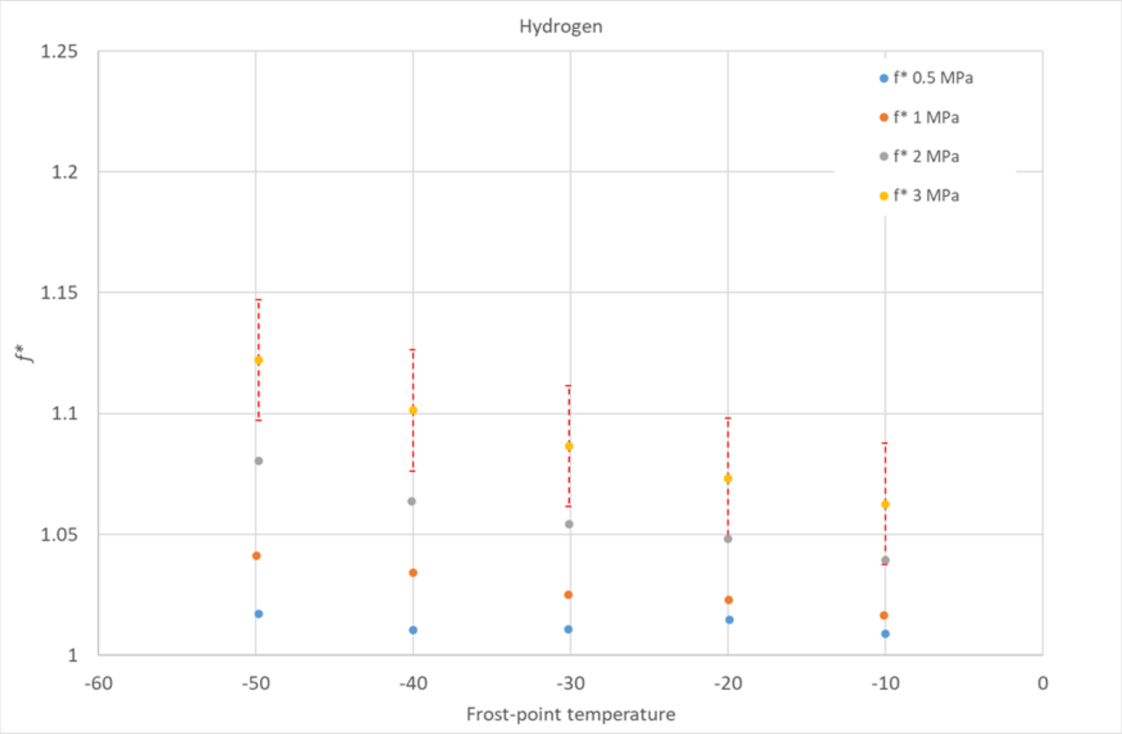
Real vapour pressure $e' = ef$

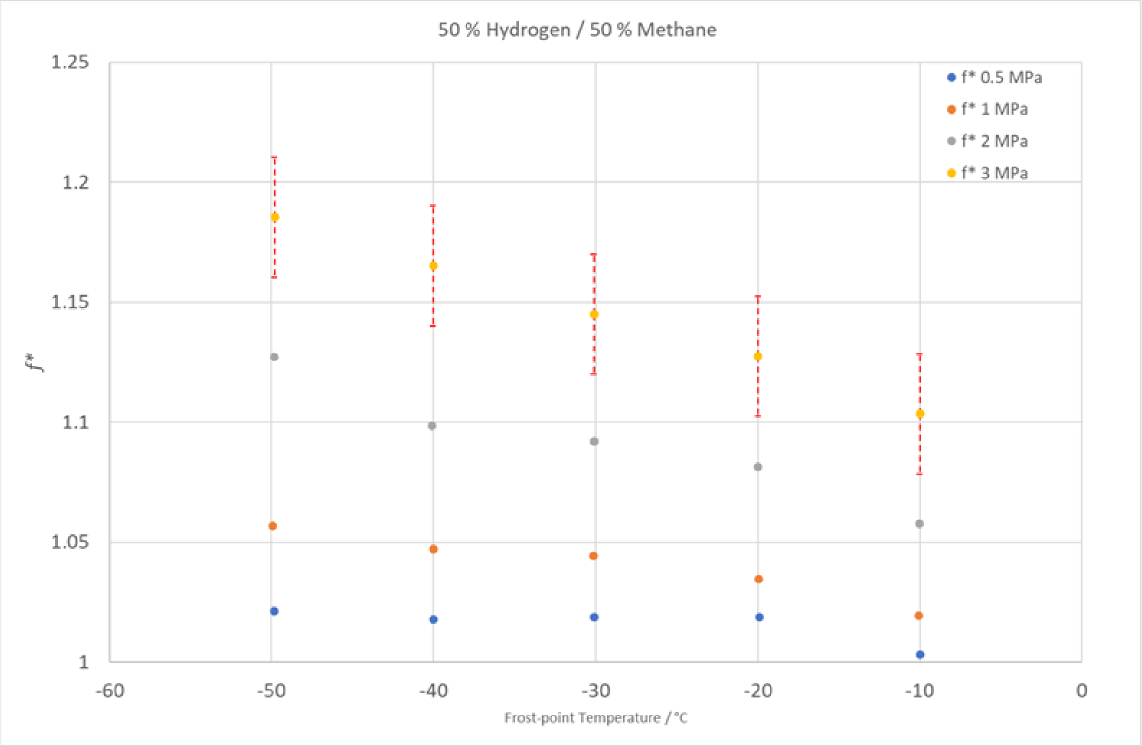
In air at -50 °C, $f \approx 1.007$, at 0.1 MPa (atmospheric pressure)
$f \approx 1.08$, at 1 MPa

Values or functions for f

- poorly known for non-air gases
- weak information for < -50 °C

Water vapour enhancement factor, NPL study, provisional data





Data measured and plotted are $f^* = f(P)/f(P_{atm})$. In fact, f^* underestimates enhancement factor by a few percent.

Conclusions

To address these challenges, we must continuously build expertise and capability:

- Improved, metrologically-sound, methods and techniques for trace water measurements;
- Development of primary standards for trace water in selected gas matrices;
- Improvement of thermophysical data knowledge of non-ideal humid gas mixtures;
- Demonstration of improved methods for trace water measurement in industrially relevant facilities (test beds).

PROMETH2O

Thank you for your attention

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