WP3 : Metrology for Hydrogen Quality from Electrical Energy Storage (HEES) by Hydrogen Back Conversion (Gas-to-Power)

WP leader: CEA
WP partners: NPL, UDC, BAM

Mefhysto Workshop, Berlin, July 3rd - 5th 2023

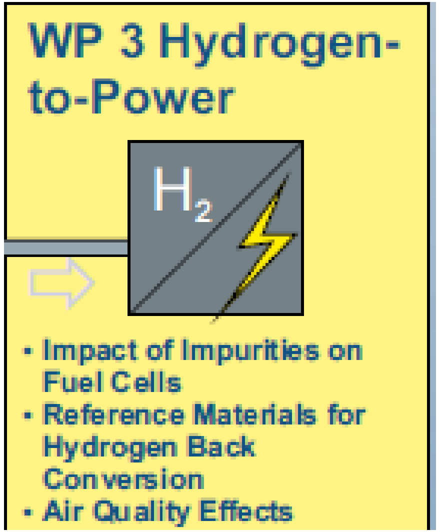
The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

WP3 Overview

Metrology for Advanced Hydrogen Storage Solutions

- **Objectives**
  - Investigate the sustainability and reliability of FC, whose performance is affected by **impurities in hydrogen and air**
  - **Quantify their impact** on PEMFC **performances and durability** at PEMFC single cell and stack levels
  - **Provide data for recommendations** for **air quality sensors** needed for monitoring FC systems;
  - **Demonstrate the methodology of contaminant measurements** on a whole hydrogen chain / **Identify contaminants on Hydrogen platforms**

- **WP3 is divided into 4 tasks**
  - Task 3.1 : General literature review, definition and preparation of gas reference mixtures
  - Task 3.2: Evaluation and quantification of the impact of relevant contaminants in H_2 supplies for PEM FC for short-term and long-term operation.
  - Task 3.3: Evaluation and quantification of the impact of relevant contaminants in Air supplies for PEM FC for short-term and long-term operation.
  - Task 3.4: Validation of a metrological chain for gas analysis using a complete demonstration H_2 platform.



Development of Relevant H_2 and Air Gas Reference Mixtures

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- **Definition of the H_2 mixtures for PEMFC**
  - Gas compositions based on:
    - ISO 14687-2 compounds in H_2 such as NH_3, H_2S, CO, new impurities and possible combinations between these contaminants.
    - Other species may be considered based on Mefhysto WP1/WP4/WP5, literature, and related projects HYCORA, HYDRAITE, MetroHyve 1 and 2, Hydrogen.
    - "ISO 14687 – like H_2" : Prepared at NPL with relevant contaminants
    - Mixtures ready to be used at CEA and NPL for PEMFC testing

Impurity	ISO 14687:2019 Grade D Limits \ µmol mol^{-1}
Water	< 5
Total Hydrocarbons (except Methane)	< 2
Methane	< 100
Oxygen	< 5
Helium	< 300
Nitrogen	< 300
Argon	< 300
Carbon Dioxide	< 2
Carbon Monoxide	< 0.2
Total Sulphur	< 0.004
Formaldehyde	< 0.2
Formic Acid	< 0.2
Ammonia	< 0.1
Halogenated Compounds	< 0.05

Development of Relevant H_2 and Air Gas Reference Mixtures

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- **Definition of the Air mixtures for PEMFC**

Contaminants	Min conc. tested	Critical value identified in litterature (ppb)	Values considered in MEFHYSTO (ppb)
NO	100-300	150	100
NO_2	100-300	150	0 (No NO + NO_2 mixture available)
NH_3	200-1000	200	100
Toluene	50-100	30	5
SO_2	10-100	10	10

At CEA : 6 gas bottles available to be diluted in the synthetic air supply

Gas	Low concentration in N_2 matrix	High concentration in N_2 matrix
Mixture	SO_2 5 ppm + 100 ppm NO	SO_2 50 ppm + 100 ppm NO
Toluene	5 ppm	0.5 ppm
NH_3	10 ppm	100 ppm

Possibility to check also periodic peak effects with x10 high concentrations

- Misz et al., Sensitivity analyses on the Impact Of Air Contaminants On Automotive Fuel Cells, *FUEL CELLS 16 (2016), No. 4, 444 – 462.*
- Talke, A. et al., Influence of Urban Air on Proton Exchange Membrane Fuel Cell Vehicles - Long Term Effects of Air Contaminants in an Authentic Driving Cycle. *J. Power Sources **2018**, 400, 556–565.*
- Schmid et al., Effects of Impurities in the Cathode Airflow on PEM Fuel Cell stacks, *Ext. Abstract A0205, EFCF2021*
- Misz, Effects, Damage Characteristics and Recovery Potential of Traffic-induced Nitric Oxide Emissions in PEM Fuel Cells under Variable Operating Conditions, FuelCells, 18 (2018), N°5, 594–601

Development of Relevant H_2 and Air Gas Reference Mixtures

• Work on the methodology for air sampling and air analysis

Key considerations

- Stability of analytes during sampling, storage and desorption
- Hydrophobicity (moisture can affect adsoption and analysis for some sorbents)
- Artifacts/blank peaks
- Breakthrough volume (limits flow rate and volume that can be sampled)
- Boiling point determines the **sorbent strength** needed

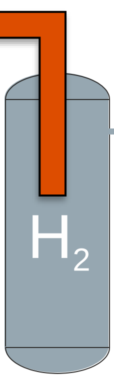
- Strong enough to retain the analytes and weak enough to efficiently release them
- For mixtures with different volatilities a multi-bed sorbents tube can be used
- Weakest sorbent must be first in sampling (to avoid irreversible adsoption of less volatile analytes on the stronger sorbents) and last in desorption

VOCs analysis

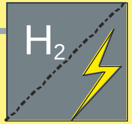
Pre-concentration

TD-GC-MS is widely used

Use of sorbents for VOCs sampling/enrichment



3 Hydrogen-to-Power



- Sustainability of Fuel Cells
- RM for Hydrogen Back Conversion
- Air Quality Effects

45 halogenated VOCs + qualitative screening for identification of other ones to identify/quantify relevant air contaminants for PEMFC

Impact of contaminants in H_2 and air supplies for PEMFC for short-term and long-term operation

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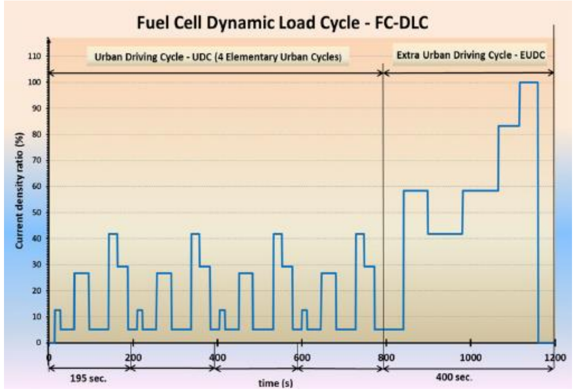
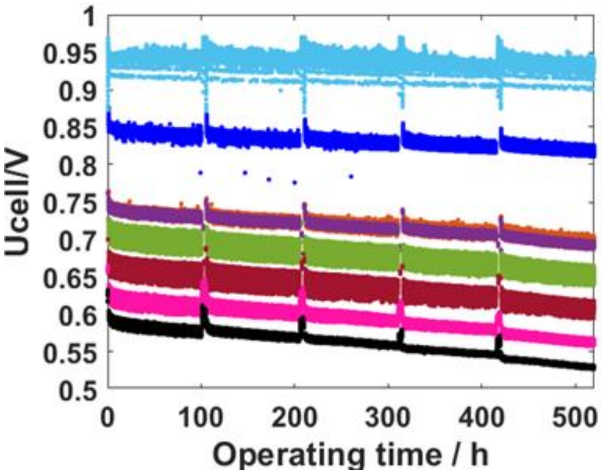
- **Strategy used in the WP for both H_2 and Air**:
  - Impact of contaminants studied at 2 main levels :
    - Small single cell under realistic operating conditions : durability study (500-1000h)
    - Short-stack (1 kW) under realistic operating conditions : protocols and short-term performances





25 cm² Single Cell voltage evolution during reference durability tests for 500 h using FC-DLC in 25 cm² single cell

Reference performance and durability data using “pure” reference gases

H_2 6.0 and Synthetic Air

Tests with contaminants planned Q3/Q4 2023 at CEA and NPL

Impact of contaminants in H_2 supplies for PEMFC for short-term and long-term operation

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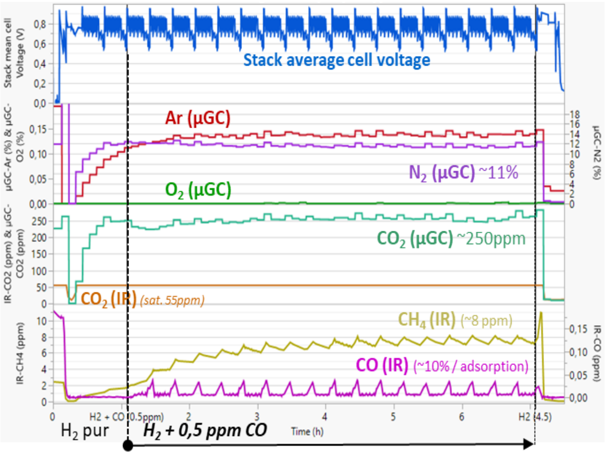
- **Study at short-stack level (~ 1 kW)**
  - **Impact of contaminants on the real-size cell** operation with special attention paid to the **combination of pollutants** and possible decontamination processes
  - **Evaluation of the efficiency** of existing testing protocols available or existing specific **operating conditions for depollution** based on the current density distribution as well as the cell voltage evolution monitoring.
  - **Determination of the reversible/irreversible pollution mechanisms** and their respective impact on both FC performances and degradations.

Stack Test Bench coupled with H_2 gas analysis



Tests planned Q3/Q4 2023
Poster about HYDRAITE results available during the WS

cea

BAM

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UNIVERSIDADE DA CORUÑA

NPL
National Physical Laboratory

Thank you for your attention !

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Metrology for Advanced Hydrogen Storage Solutions

New metrology for Hydrogen Quality from Power-to-Hydrogen and from Electrical Energy Storage (HEES) by Hydrogen Back Conversion (Gas-to-Power)

Paul Carroll
(National Physical Laboratory, London, UK)

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Session Overview

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Metrology for Advanced Hydrogen Storage Solutions

16:00–16:10	**New metrology for Hydrogen Quality from Power-to-Hydrogen and from Electrical Energy Storage (HEES) by Hydrogen Back Conversion (Gas-to-Power)**	Paul Carroll (National Physical Laboratory, London, UK)
16:10–16:20	**Assuring Safety and Quality of Hydrogen production**	Stephan Zuijdendorp, Global Sales, Process Sensing Technologies, Ely, United Kingdom
16:20–16:30	**Metrology for Hydrogen Vehicles2 – Overview of project achievements**	Thomas Baquart, (National Physical Laboratory, London, UK)
16:30–17:30	**Workshop** (Quality from Water Electrolysis, Online Gas Analysis, Reference Analytics, Impact of Impurities on Fuel Cells, Reference Materials, Air Quality Effects)	Experts from the MefHySto consortium
16:30	Introduction to workshop	Paul Carroll, (National Physical Laboratory, London, UK)
16:30-16:50	**Topic 1:** Electrolysers / effects of impurities on fuel cells. 10 minute presentation followed by panel discussion.	Jonathan Goh, (National Physical Laboratory, London, UK) and Fabrice Micoud (Commissariat à l'Énergie Atomique et aux Énergies Alternatives, Grenoble, France)
16:50-17:10	**Topic 2:** Online Gas Analysis for quality measurement / reference analytics. 10 minute presentation followed by panel discussion.	Paul Carroll, (National Physical Laboratory, London, UK)
17:10-17:30	**Topic 3:** Reference material production / reference analytics. 10 minute presentation followed by panel discussion.	Ziyin Chen, Thomas Baquart, (National Physical Laboratory, London, UK), Michael Maiwald, Dirk Tuma, BAM, Berlin, Germany

WP1: New Metrology for Hydrogen Quality from Power-to-Hydrogen

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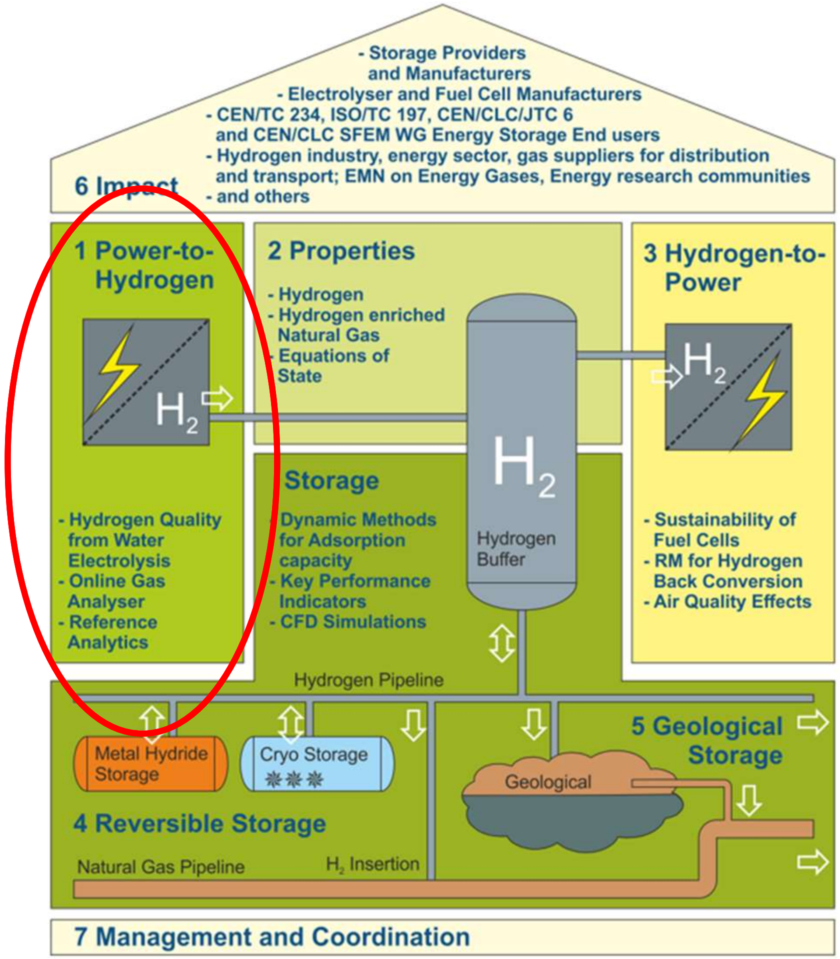

- Internal funded partners

NPL National Physical Laboratory | PTB Physikalisch-Technische Bundesanstalt Braunschweig und Berlin | cea

- External funded partners

DBI

WP1 Objectives

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- Better understanding of the parameters influencing water electrolysis under process conditions.
- Detailed investigations on energy processes and load conditions are still lacking, including short-term peak energy loads of up to 200 %. These must be handled safely in order to prevent quality problems or damage to fuel cells (FC) and peripheral equipment.
- Go beyond the state of the art by investigating the quality of hydrogen produced from PEM water electrolysis during rapidly imposed transient use periods.
- This will be done with online gas analysers used for measuring key impurities such as water vapour and oxygen calibrated against standards developed by project partners.

WP1: New Metrology for Hydrogen Quality from Power-to-Hydrogen

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Task 1.1: New metrology for realisation and measurement of key impurities in hydrogen, with fast response times

develop new metrology for the measurement of key impurities in hydrogen (including water vapour and oxygen) produced from PEM water electrolysers with fast response times of a few or tens of seconds (i.e. the timescale of surges in electricity demand and supply).

Task 1.2 Testing and validation of instruments for measuring key impurities in hydrogen

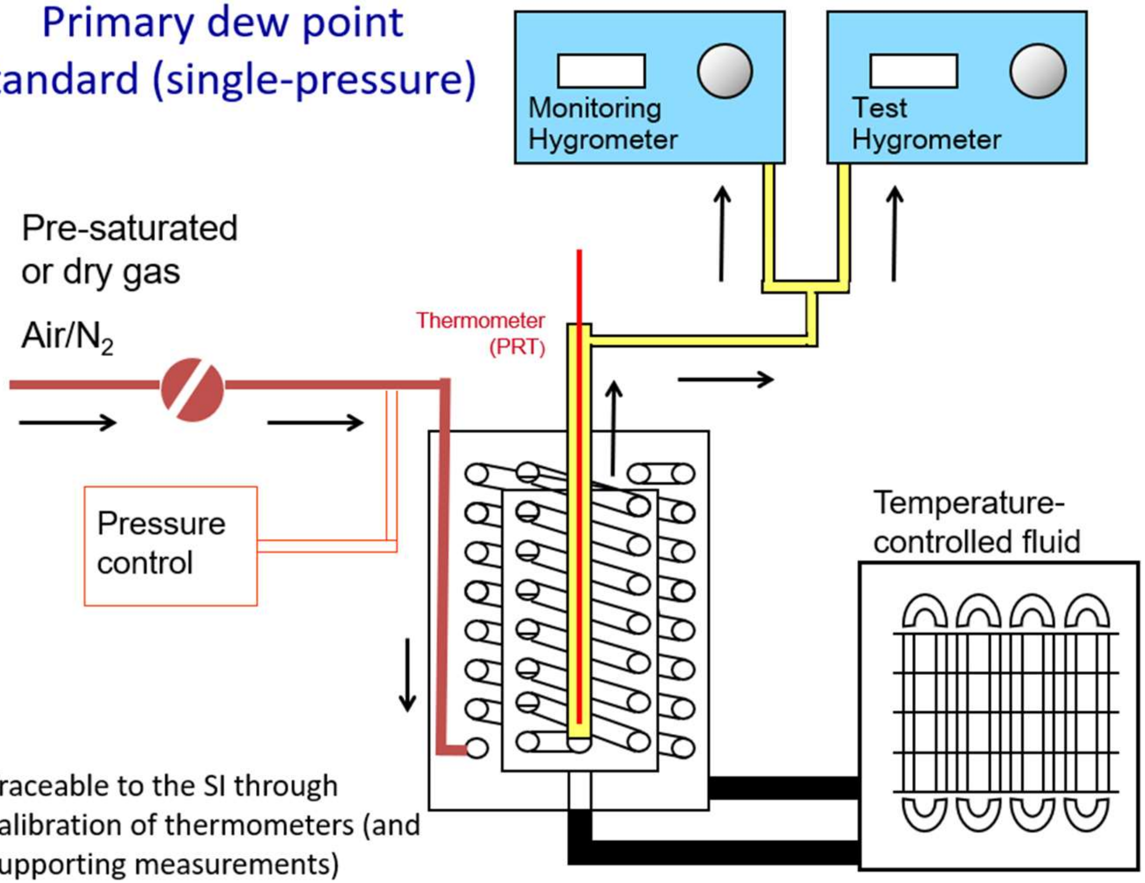
validate the performance of instruments for measuring key impurities (principally water vapour and oxygen) in hydrogen including the spectroscopic method developed and validated in Task 1.1 and existing online gas analyser instruments with suitably fast response times.

Task 1.3: Trials of rapid response analysis of key contaminants of hydrogen from electrolysis

demonstrate measurements of contaminants in-situ in hydrogen generated from electrolysis. This will be done by trialling the PEM water electrolyser test system developed in Task 1.1 and the other instruments for in-process measurement of contaminants in hydrogen characterised in Task 1.2, as well as a micro GC. Results presented in workshop later today.

NPL Dew-point hygrometer calibration standard

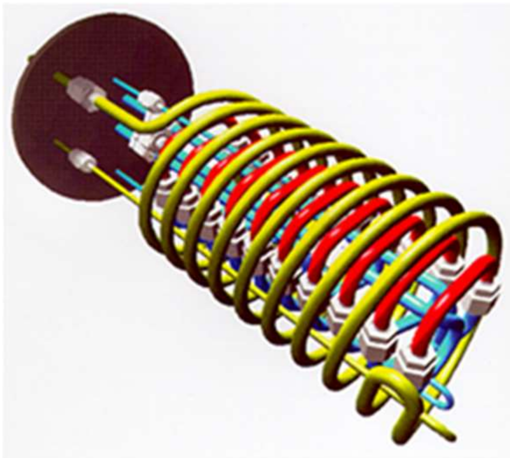
Primary dew point standard (single-pressure)



Traceable to the SI through calibration of thermometers (and supporting measurements)

NPL Multi-gas, Multi-pressure primary standard humidity generator

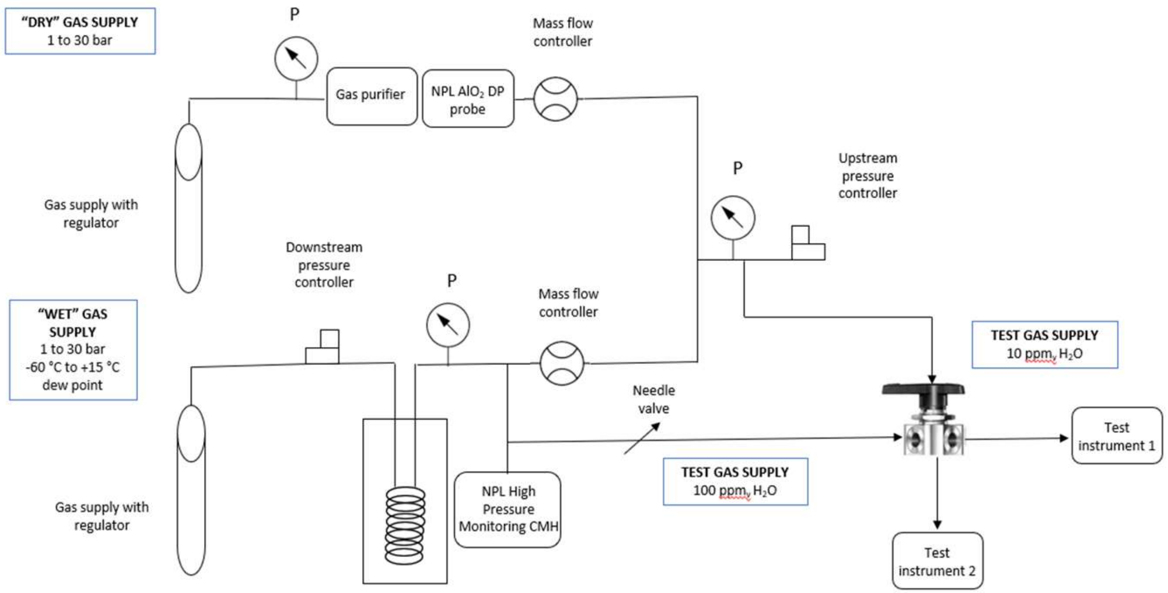
- Moderately inert gases (e.g hydrogen, methane, argon)
- Pressures up to 3 MPa (30 bar)
- Dew/frost point range -60 °C to +15 °C   (k = 2 expanded unc. = 0.12 °C)
- Hybrid generator: calibration in single pressure dew-point mode
- Ability to mix wet & dry gases using array of mass flow controllers



NPL humidity response time testing facility

Source: Swagelok

- 4-way valve used to make fast step changes in water vapour in conjunction with NPL Multi-gas, Multi-pressure Primary Standard Humidity Generator. Volume of path lengths between valve and test instruments kept as small as possible.
- Dilution of "wet" gas with "dry" gas using MFC flow-mixing approach means two dynamic sources of different humidities can be simultaneously generated with a range of water content values accessible.



NPL humidity response time testing analysis

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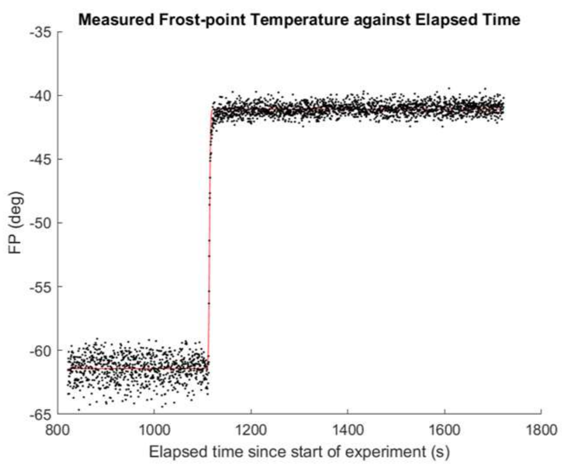
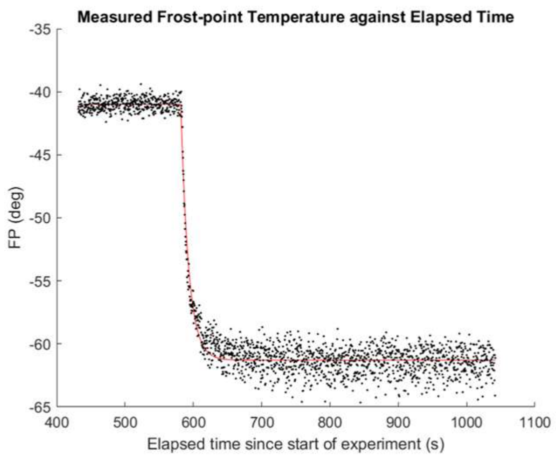




Functions written by NPL Data Science group in MATLAB perform fitting to measured data and estimate t_{90} rising and falling values.

Sigmoid function fit analysis for rising series,

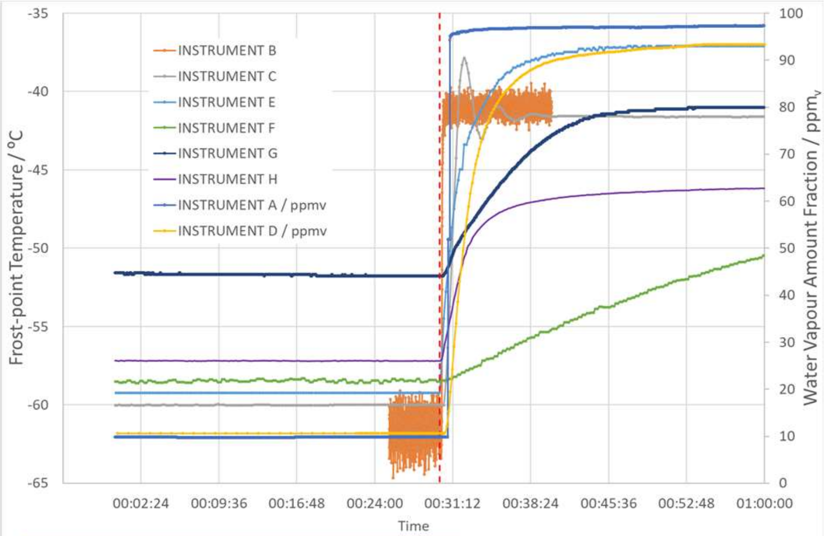
Exponential decay function for falling series.

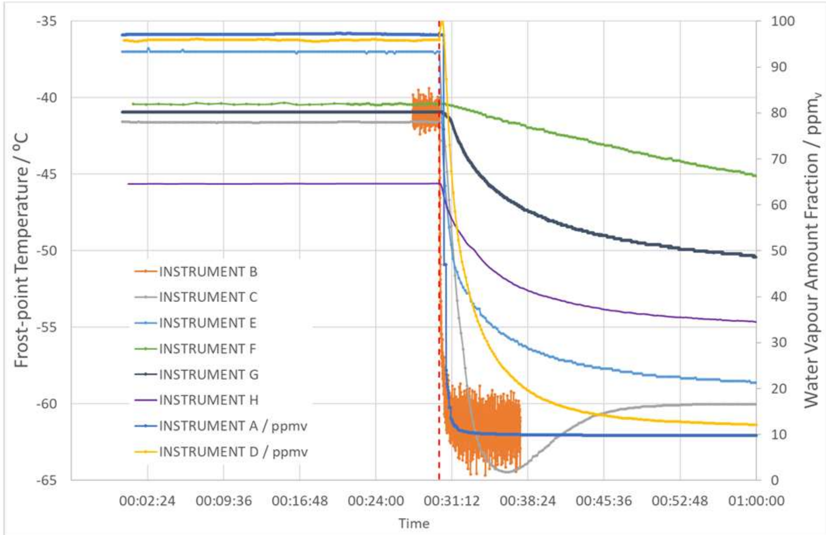
Uncertainty estimate in calculated response time estimate due to scatter and curve fitting is also evaluated.

Eight instruments loaned from collaborators tested for pressure and background gas measurement error dependency as well as response time analysis. Some example results and their implications to quality measurements discussed in workshop later.

Sensing principles include: chilled-mirror hygrometer, metal-oxide dew point probe, water vapour spectrometer, surface acoustic wave, fibre optic method sensing principle, electrolytic P_2O_5.

- **NPL Humidity and NPL Gas Metrology:** Using input from (A1.2.1), (A1.2.2) and the NPL primary (dynamic) humidity generation facilities, NPL will assess the response time (performance) of online gas analysers and sensors of water vapour and oxygen. NPL will use the step change test facility developed in A1.1.2 for the assessment**. (A1.2.4)**





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

Instrument	Manufacturer specification response time / s
INSTRUMENT A	Met
INSTRUMENT B	Met
INSTRUMENT C	Not given
INSTRUMENT D	Not given
INSTRUMENT E	Not given
INSTRUMENT F	Not given
INSTRUMENT G	Not met
INSTRUMENT H	Not met

Instrument	t_{90} response time / s
INSTRUMENT A	28.32
INSTRUMENT B	26.28
INSTRUMENT C	117.9
INSTRUMENT D	417.8
INSTRUMENT E	449.5
INSTRUMENT F	16822
INSTRUMENT G	3452
INSTRUMENT H	2580

t_{90} for INSTRUMENT F = 280 minutes

Task 1.1 – (A1.1.2) NPL O_2 sensor response time testing set up

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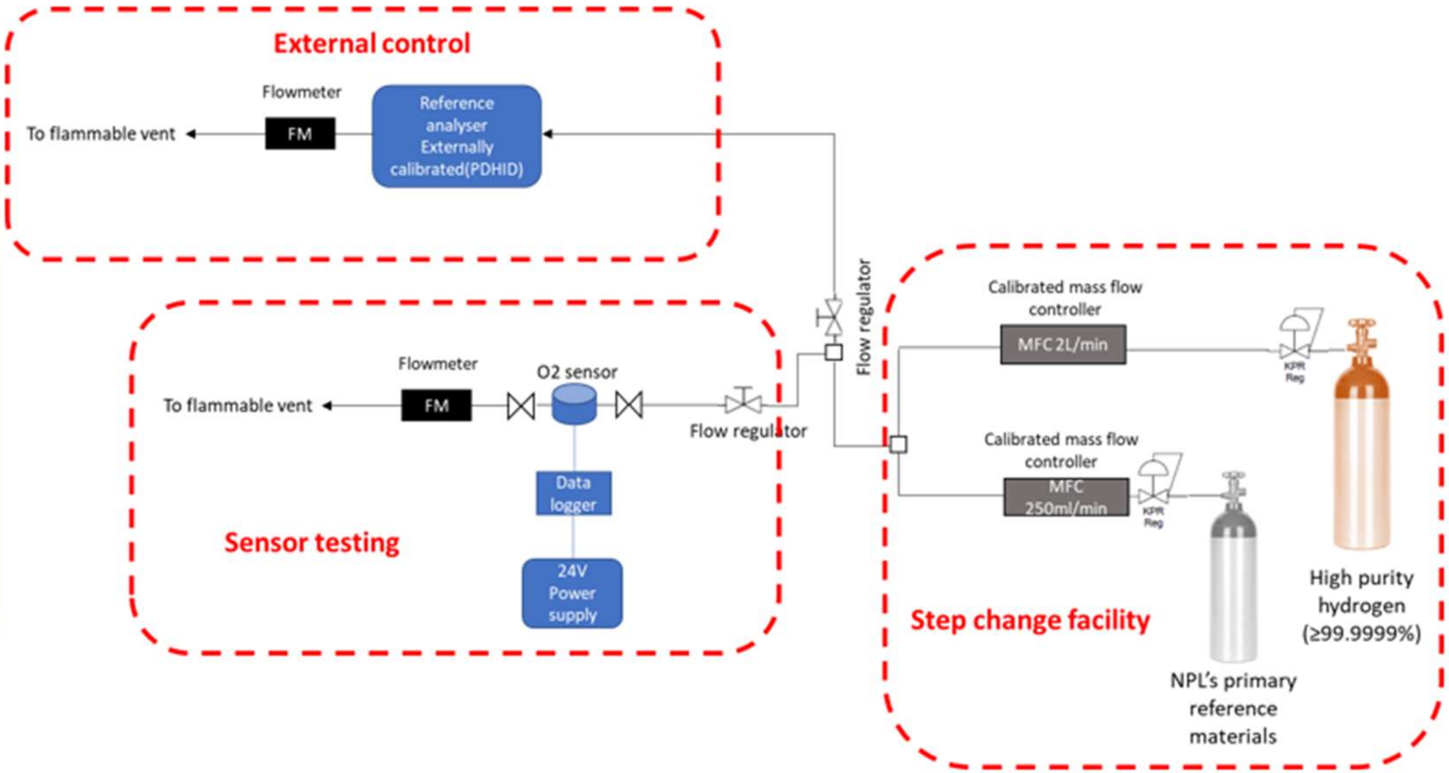
- NPL developed a bespoke step change facility for sensors validation
  - Rapid change of amount fraction;
  - Traceability to NPL's PRM;
  - Flexible flow rate;
  - External validation of amount fraction via a parallel line to NPL calibrated gas analyser.

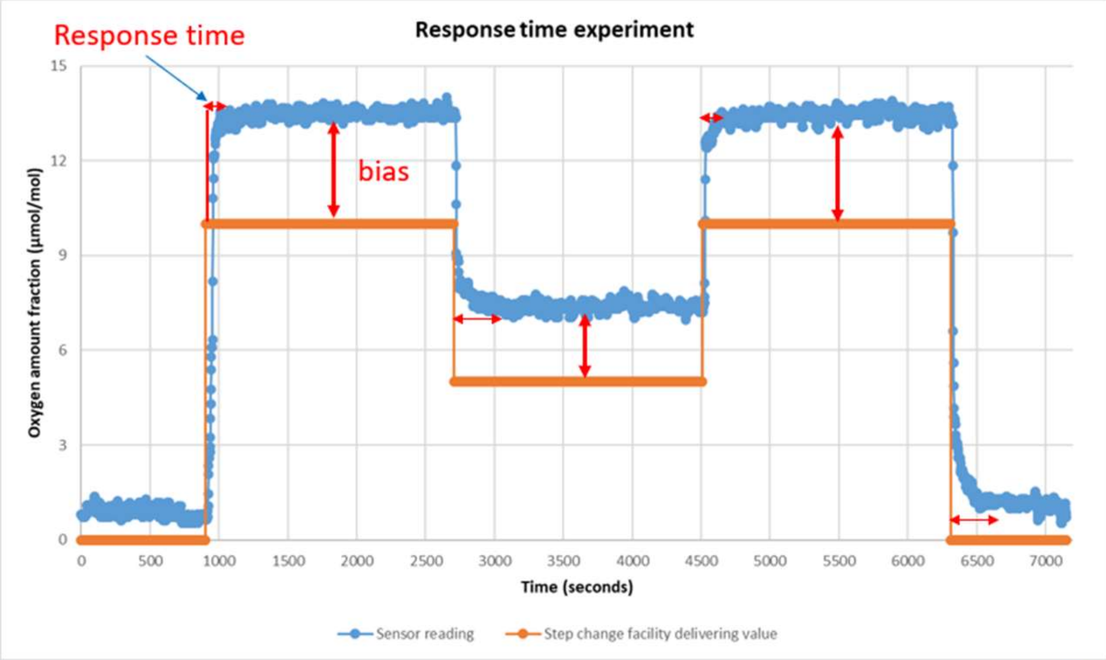


Achievements: compatible with most contaminants in H2 (i.e., O_2 from 0.5 to 20 µmol/mol); fast response (< 20 seconds)

Example of experimental results

Experimental conditions:

- Oxygen sensor A
- Amount fraction 0, 5, 10 µmol/mol oxygen in hydrogen
- Response time: < 5 sec from NPL Step change facility
- Pressure: 1.04 bar
- Flow rate: 0.44 L/min
- Temperature: 20 °C



- ➢ The sensor A responded rapidly to the change of oxygen amount faction in hydrogen gas
- ➢ Significant bias observed (nearly 25 to 30%) between actual reading from sensor and theoretical value
- ➢ Impact: (+) fast response from sensor achieved / (-) inaccurate information to end users
- ➢ Further modifications/improvements for sensors: improve trueness.

Task 1.1 – (A1.1.2) NPL O_2 sensor response time testing results

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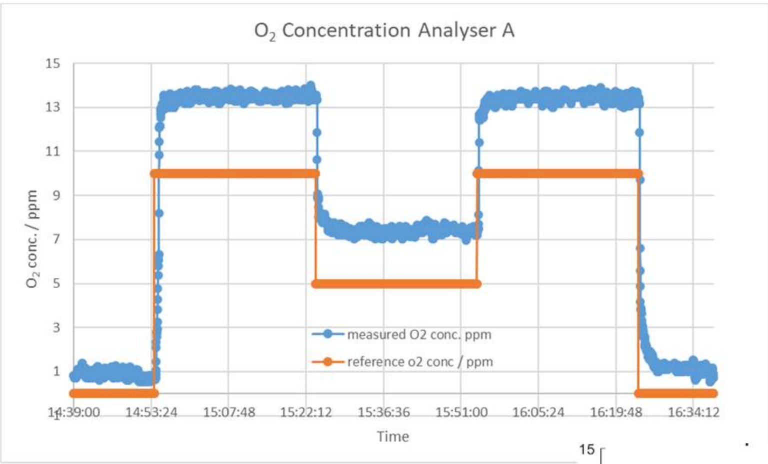
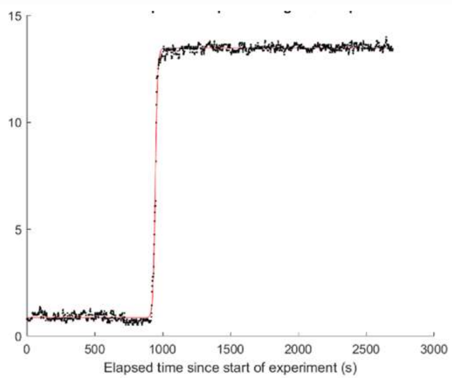
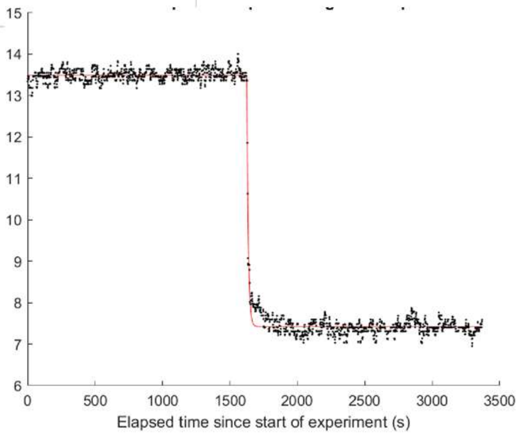


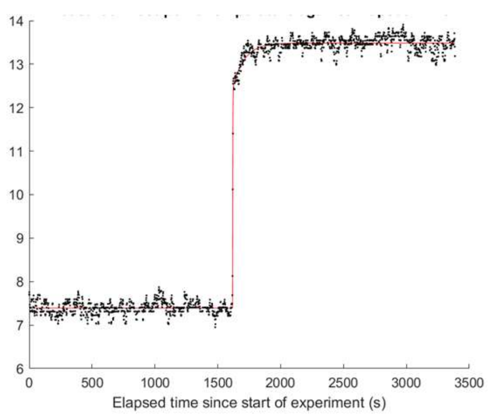
Step change O_2 / µmol mol^{-1}	Time / s
0 – 10 rising	73
5 – 10 rising	29
10 – 0 falling	76
10 – 5 falling	35



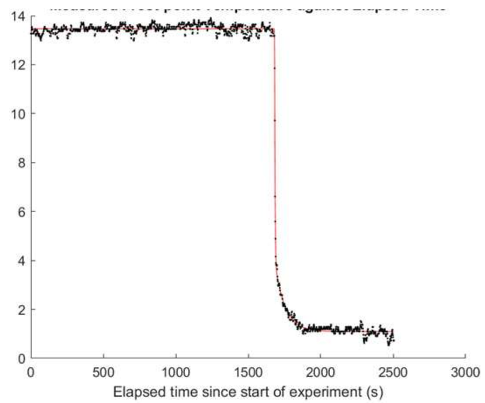
0 – 10 µmol mol^{-1}



10 – 5 µmol mol^{-1}



5 – 10 µmol mol^{-1}



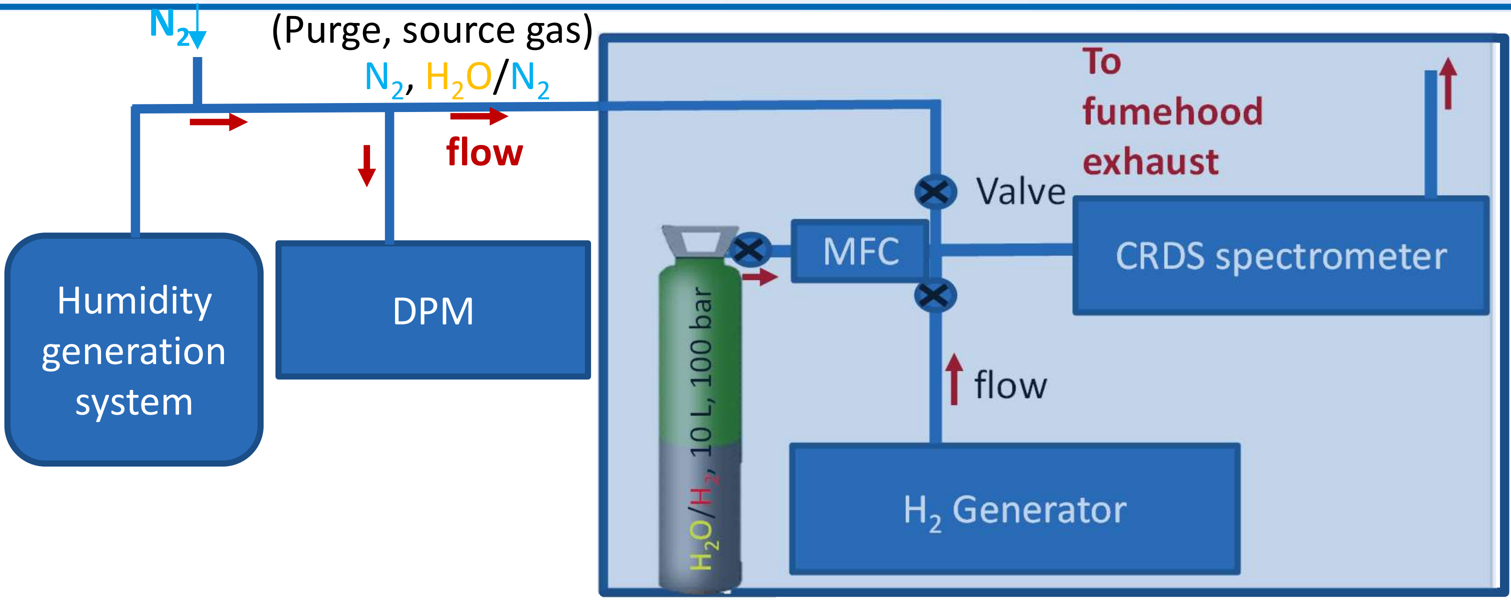
10 – 0 µmol mol^{-1}

Task 1.1 - A1.1.1 Progress month 22

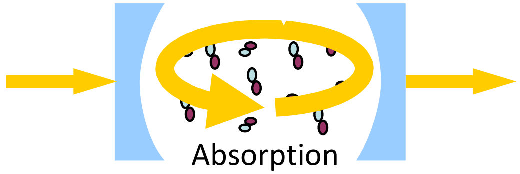
PTB will develop a metrologically compatible laser-spectrometric measurement method for fast H_2O impurity measurements in H_2. (A1.1.1)

- **PTB:**
- Tiger Optics Halo HALO-RP has been selected as a suitable instrument to adapt for the application specificities.
- The measurement principle for this instrument is Cavity Ring-Down Spectroscopy (CRDS). Maximum measurement range 10 ppm H_2O.
- Trial measurements to be made at PTB with nitrogen background gas prior to arrival of water vapour reference cylinders in Hydrogen from **NPL Gas Metrology.**
- Reference cylinders prepared by **NPL Gas Metrology** with 2 µmol mol^{-1} , 5 µmol mol^{-1} and 10 µmol mol^{-1} water vapour in hydrogen amount fractions and sent to PTB.
- Mixtures validated against NPL gravimetric standards and NPL humidity standards.

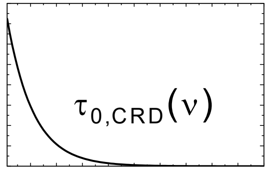
PTB Progress Task 1.2 – (A1.2.6)



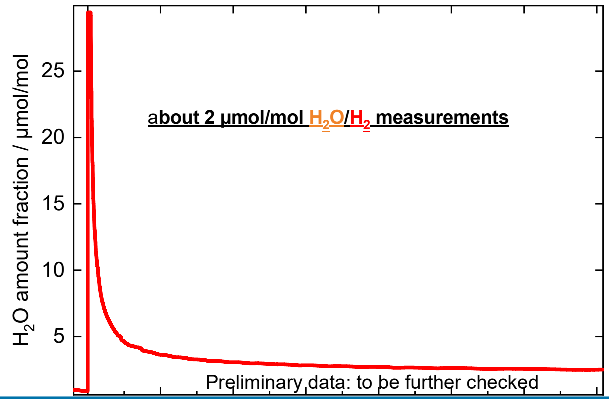
Cavity Ringdown spectroscopy (CRDS)



Ringdown time



- Measurements have been performed with the mixtures from A1.2.2 (provided by NPL: 2, 5 10 µmol/mol H_2O in H_2).



PTB Progress Task 1.2 – (A1.2.6)

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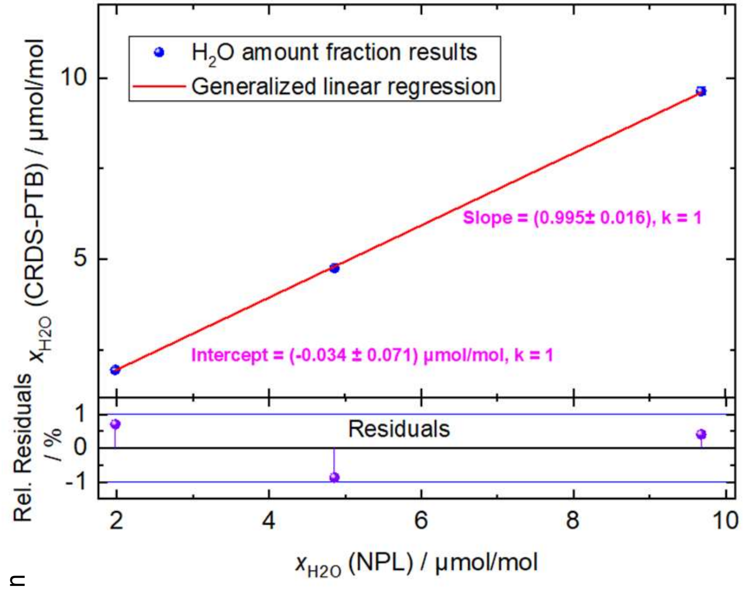
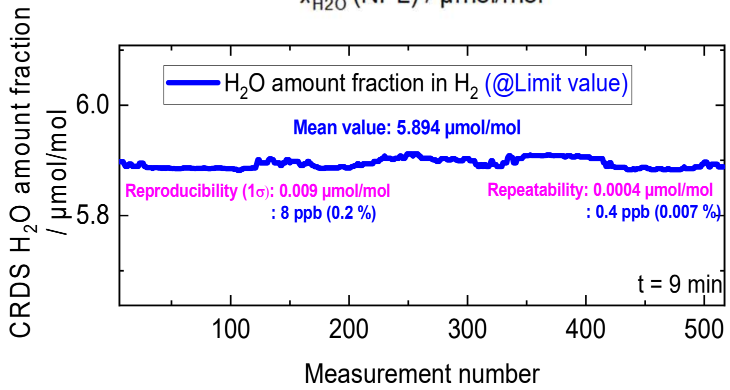
- Measurements are done employing a laser spectrometric method based on **cavity ring down spectroscopy –CRDS** for H2O impurity measurements in H2.
- Measurements with H_2O in H_2 mixtures provide by NPL demonstrates a good linearity of the method/instrument.
- At the ISO14687 limit value (5 µmol/mol H_2O in H_2), the reproducibility of the measurements is 0,008 µmol/mol (0.2 %, 1σ, over 9 minutes).

Contaminant in H_2	H2O-Limit in H2 (ISO14687)
H_2O	5 µmol/mol





Task 1.1 – Establishment of PEM water electrolyser test systems

NPL National Physical Laboratory will establish a PEM water electrolyser test system (single cell) with online impurity measurement at the cathode. (A1.1.3)

cea will perform single cell testing to study the impact of operating conditions and transient profiles on the cell performances and on the quality of produced hydrogen with online sensor. (A1.1.3)

CEA: PEMWE testing at single cell level test bench specifications

- 25 cm² single setup, Circular active area,Titanium monopolar plates
- Titanium foam as porous layer at the anode
- Gas Pressure : up to 10 bar abs.
- Cell temperature: up to ca. 80°C (external heating) + water supply (0-1000 mL/h) heating.
- Current supply: 0-100 A, Gas flow rates: 41 Nl/h for H_2 and 20 Nl/h for O_2

Commercial electrolyser Hogen S20 specifications

- 10 cell-stack, Stack current can be controlled by the CEA control-command software
- No internal H_2 purifier, Drying by 2 zeolite units (regenerated with dry H_2 bypass by alternative operation)
- Asymmetrical operation: atmospheric pressure at the anode / 15 bar at the cathode

- Gas analysis for %H_2 in O_2 by catharometer equipment but not really precise (drifts in time due to “wet gas”)
- µGC available for more precise measurement H_2 in O_2 and O_2 in H_2 but only periodic sampling.
- Gas mixtures were obtained to calibrate sensor in the electrolyser at CEA after it was re-started.

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Metrology for Advanced Hydrogen Storage Solutions

Thank you! Questions?

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Metrology for Advanced Hydrogen Storage Solutions

Online Gas Analysis for hydrogen quality measurement and reference analytics

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Task 1.2: Testing and validation of instruments for measuring key impurities in hydrogen

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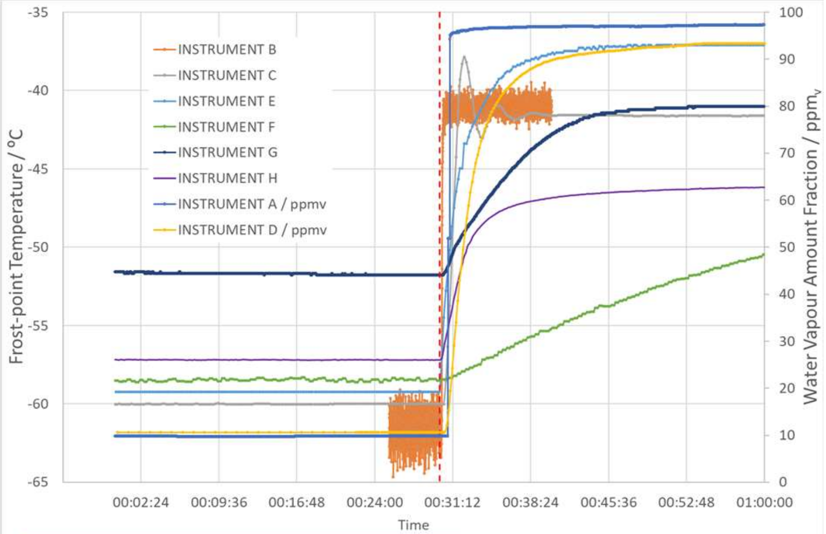
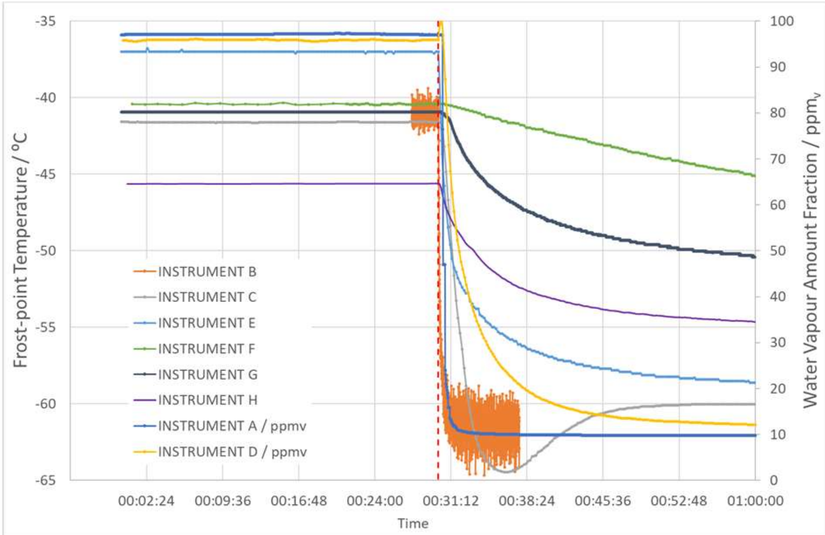
- **NPL Humidity and NPL Gas Metrology:** Using input from (A1.2.1), (A1.2.2) and the NPL primary (dynamic) humidity generation facilities, NPL will assess the response time (performance) of online gas analysers and sensors of water vapour and oxygen. NPL will use the step change test facility developed in A1.1.2 for the assessment**. (A1.2.4)**





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

Instrument	Manufacturer specification response time / s
INSTRUMENT A	Met
INSTRUMENT B	Met
INSTRUMENT C	Not given
INSTRUMENT D	Not given
INSTRUMENT E	Not given
INSTRUMENT F	Not given
INSTRUMENT G	Not met
INSTRUMENT H	Not met

Instrument	t_{90} response time / s
INSTRUMENT A	28.32
INSTRUMENT B	26.28
INSTRUMENT C	117.9
INSTRUMENT D	417.8
INSTRUMENT E	449.5
INSTRUMENT F	16822
INSTRUMENT G	3452
INSTRUMENT H	2580

t_{90} for INSTRUMENT F = 280 minutes

Response time results implications and good practice

- A slow response to a humidity change from an online monitoring sensor would result in delays to measurements of the true moisture value.
- Process monitoring would be slow to react resulting in potential gas quality implications or wasted energy on needless over-drying.
- **Sensor response:**
- Rising or falling step change – t_{90} significantly faster for rising changes for all instruments tested
- Sensing principle
- Measurement interval of instrument / logging software (ranged from 0.3 s to 10 s)
- Ambient temperature (NPL can vary this using environmental chambers)

- **System related:**
- Volume of connecting pipework / housing of sensor
- Flow-rate of gas to sensor

Task 1.2: Testing and validation of instruments for measuring key impurities in hydrogen

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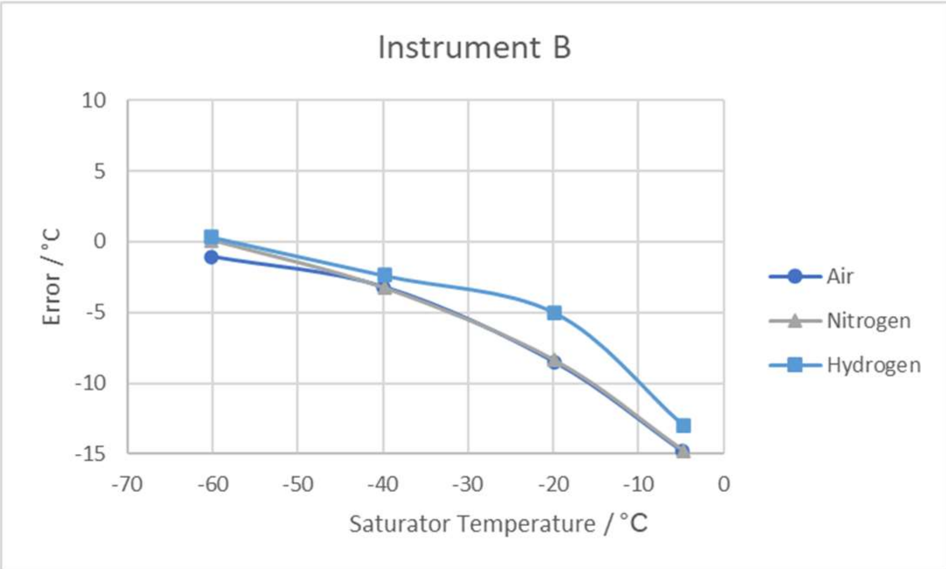
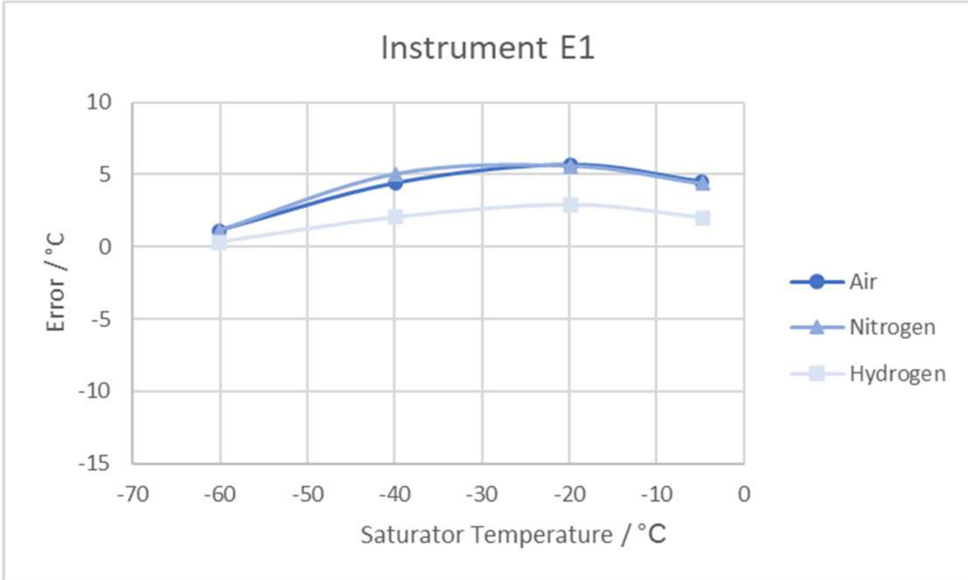
NPL Humidity: will assess at least four commercially available instruments for measuring water vapour, to evaluate influence of pressure and **of hydrogen** as background gas using the gas mixtures and the NPL Multi-gas, Multi-pressure Humidity Generator (A1.2.3)





Note: Instruments shown only recommended for use at atmospheric pressure

Task 1.2: Testing and validation of instruments for measuring key impurities in hydrogen

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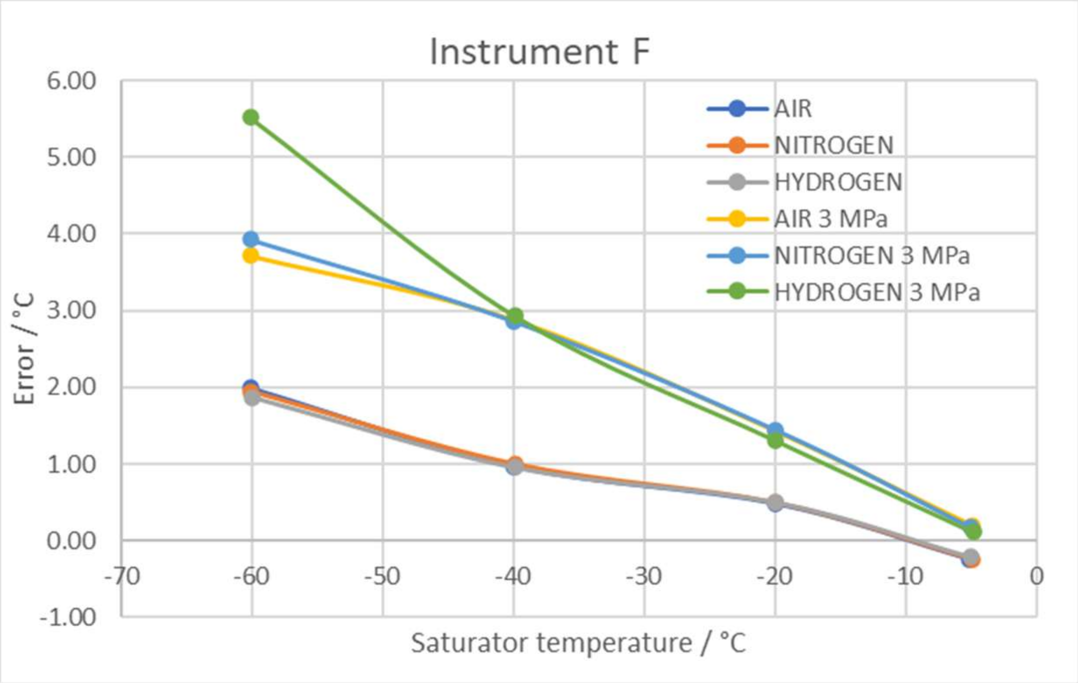

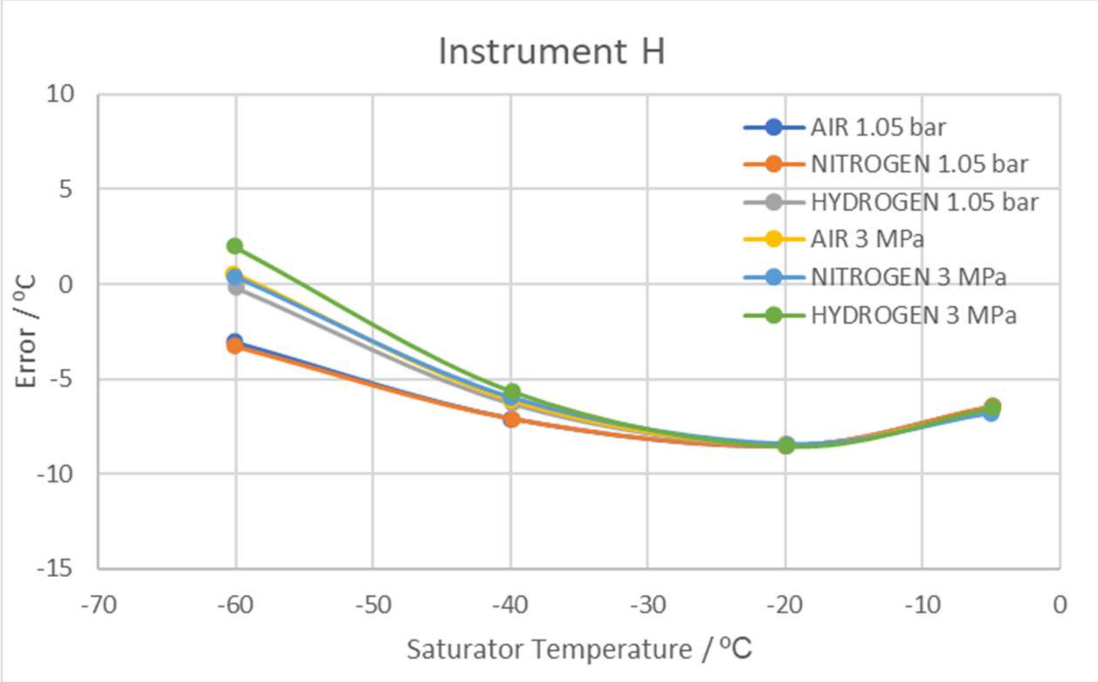

Example results of instrument long-term drift

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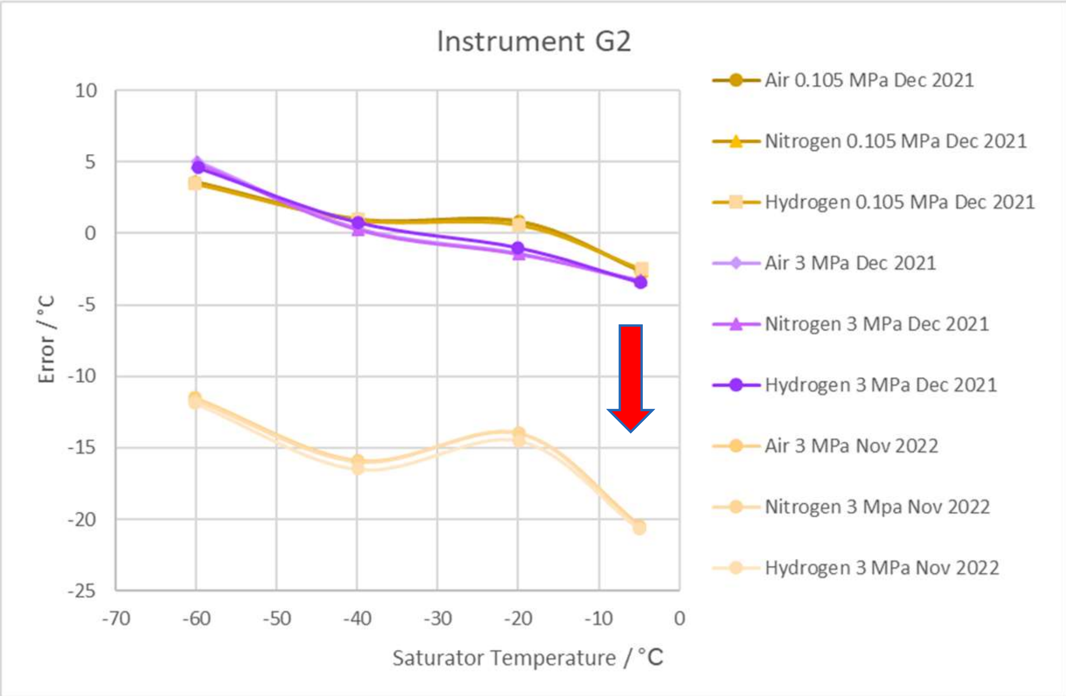

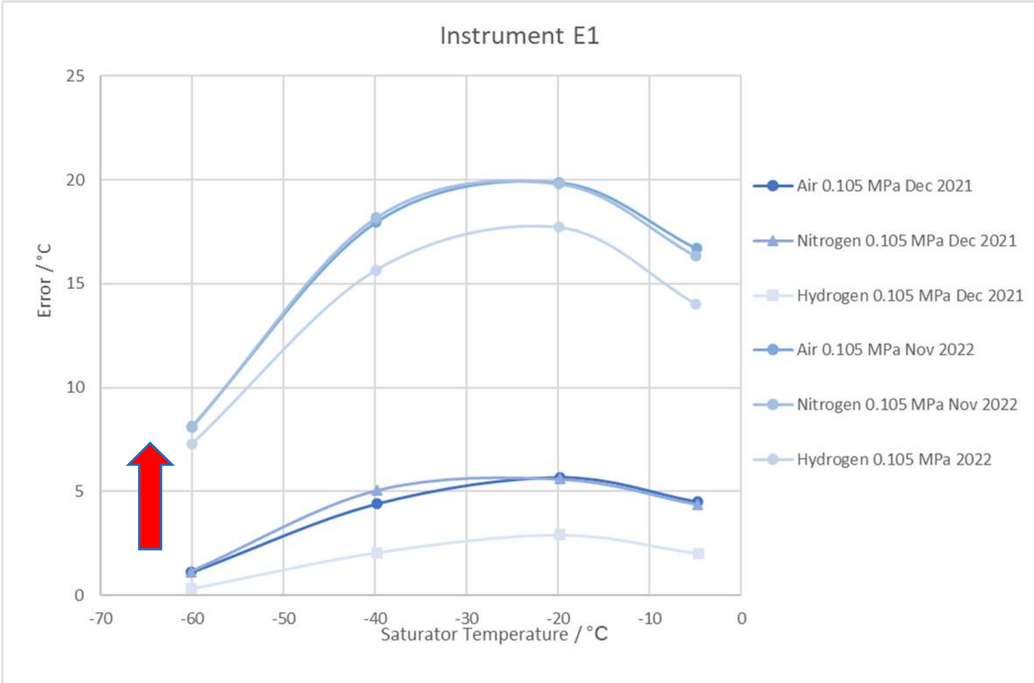

Error drift towards under reading

Error drift towards over reading

Recommendations when requesting hygrometer calibrations:

- Use a laboratory with ISO 17025 accreditation for humidity calibration in the relevant range
- Request that the calibration is in the working units of the hygrometer e.g. dewpoint temperature (°C) or volume fraction (ppm_v)
- Request at least three points covering minimum and maximum expected humidity values of the process being monitored
- If possible, request that calibration is performed in the background gas and the pressure the hygrometer would experience during service
- Request an “as-found” calibration of the hygrometer at the end of service to assess long-term drift.

- *Good Practice Guide: Calibration and use of humidity sensors for hydrogen refuelling station applications:*
- www.sintef.no/globalassets/projectweb/metrohyve-2/d5-a3.2.2-good-practice-guide-on-calibrating-commercial-humidity-sensors.pdf

Task 1.2: Testing and validation of instruments for measuring key impurities in hydrogen

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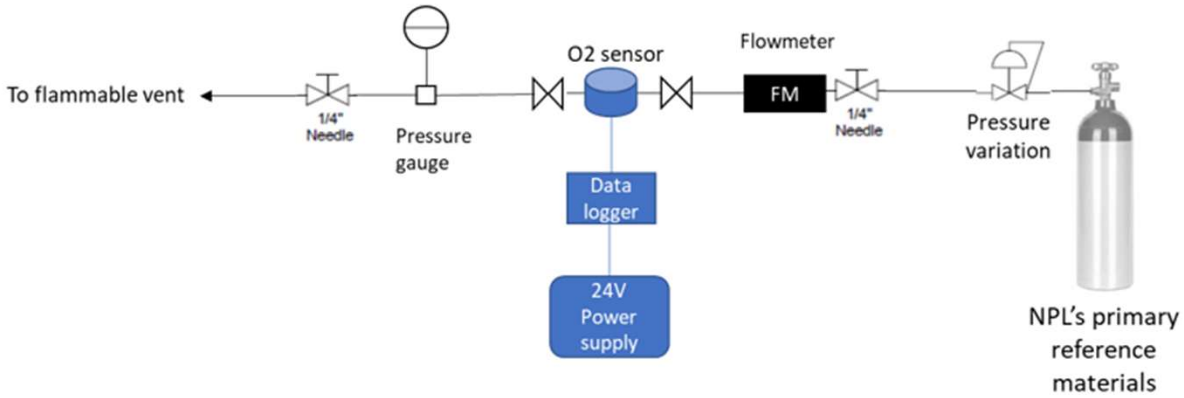
NPL Gas Metrology: will assess at least two commercially available instruments for measuring oxygen, to evaluate influence of pressure, linearity, (A1.2.3)

NPL experimental setup



- ❑ Current capability: 0 – 20 barg depending on sensor specification
- ❑ Experiment test realised from 0-1.6 barg at 5 µmol/mol oxygen in hydrogen on 2 different sensor types

Task 1.2: Testing and validation of instruments for measuring key impurities in hydrogen

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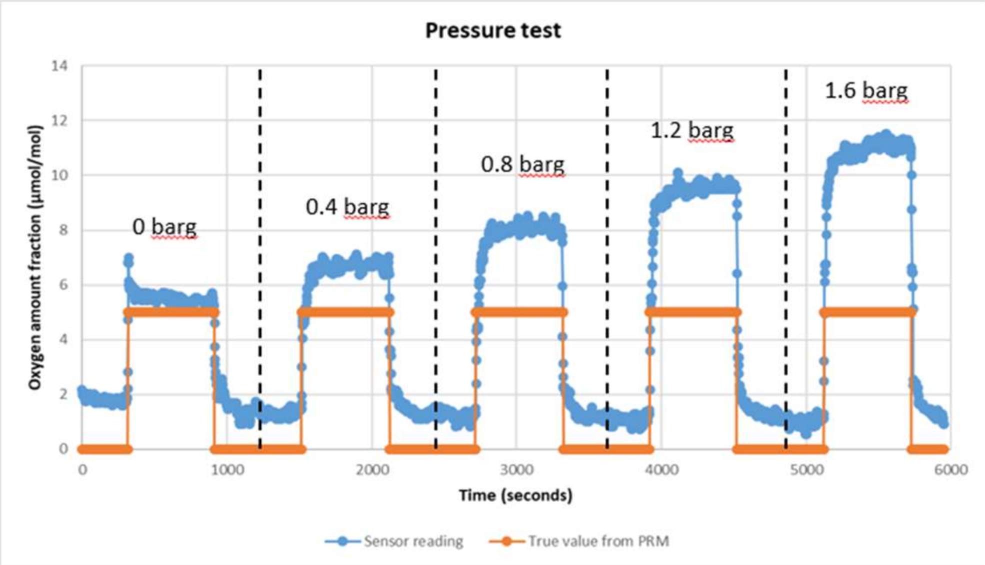
NPL Gas Metrology: (A1.2.3)

Experimental results of pressure test which was conducted with a primary reference material (5 ppm O_2 in H_2).

- ✓ The system pressure was increased from atmospheric pressure to 2.6 bar
- ✓ Between each experiment under different pressure, the system was reduced to atmospheric pressure and purged with pure hydrogen to prevent any interference.
- ✓ The flowrate was adjusted to a constant (0.4 L/min)



Note: Manufacturer's specification states only to be used at atmospheric pressure only !

Highlights:
- impact on sensor accuracy observed due to small pressure changes
    - Response x 2 from atmospheric pressure to 2.2 bar
- Other sensors under evaluation – looking for new sensor manufacturer feedback or joint activity

Task 1.3: Trials of rapid response analysis of key contaminants of hydrogen from electrolysis

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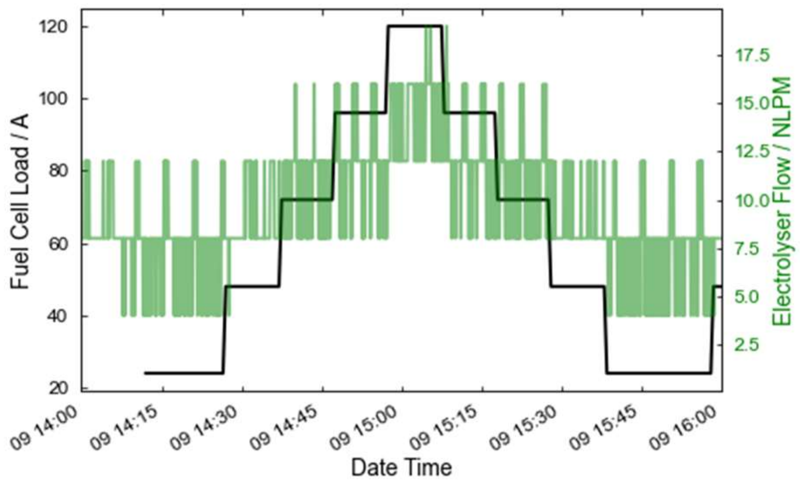
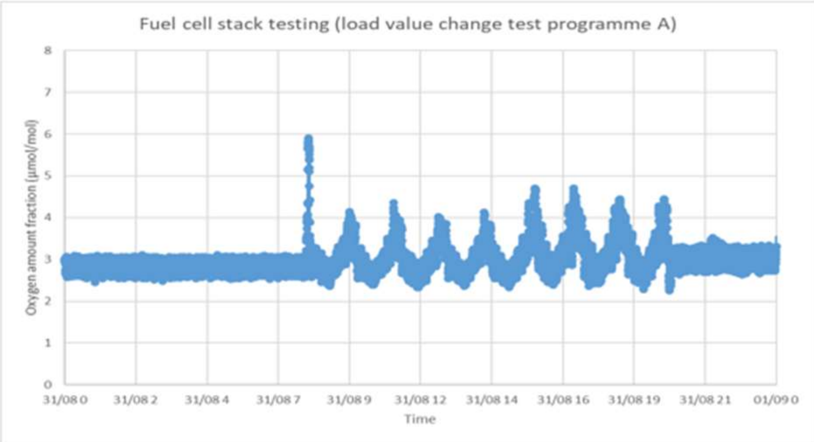
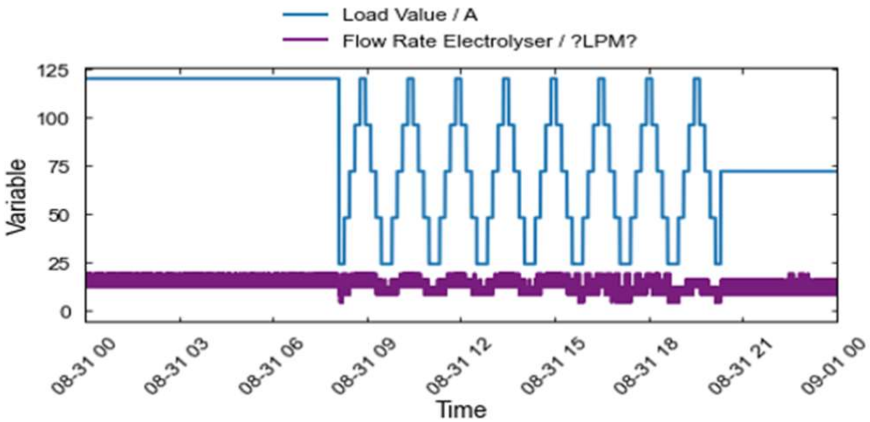
- **(A1.3.1) NPL**, CEA, PTB and DBI will develop protocols for laboratory and field trials of the spectroscopic method (A1.1.1) and validated in A1.2.6, together with the online gas analyser instruments characterised in A1.2.3, A1.2.4 and A1.2.5.

NPL			
Production			
Equipment	Hogen S Series 2 Hydrogen Generator S40		
Max Rate	1.05	Nm3/h	
Max Pressure	14	barg	
Purity	99.9995	%	
	< 5 ppm water (-65 deg C dew point atmospheric pressure)		
	< 2 ppm N2		
	< 1 ppm O2		



Application of sensor in real life situation: electrolyser





- Lack of rapid response analyser for oxygen at low µmol/mol amount fraction
  - Sensor are good option to monitor such changes for oxygen or water amount fraction
- Sensor response vary with electrolyser load change
  - Real change or Change related to operation parameters of the electrolyser (pressure, temperature, flow rate)?
- Importance to understand the rapid changes of electrolyser parameters in term of hydrogen quality
  - Is the change related to metrological issue or to hydrogen quality change from the system?
- Further works:
  - monitoring all electrolyser gas parameters (pressure, flow variation)
  - correlate the results of the study (i.e., pressure impact accuracy) with real life measurement and conditions

Task 1.3: Trials of rapid response analysis of key contaminants of hydrogen from electrolysis

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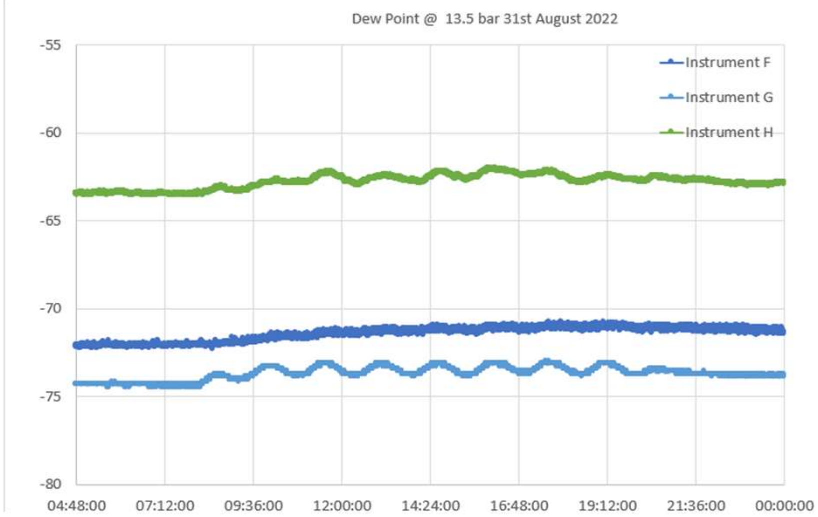
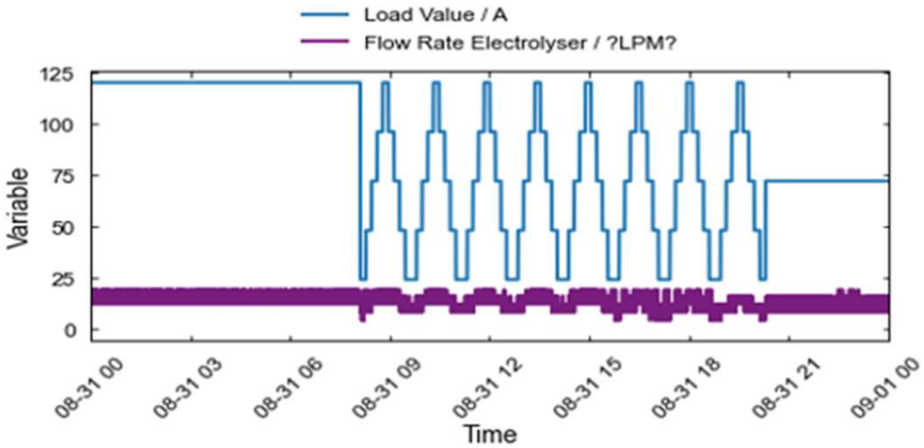
- Dew-point temperature measurements made of Hogen electrolyser H_2 at 1.35 MPa.
- Measurements corrected for error found during NPL calibration.
- Equivalent water vapour amount fraction values < 1 $\mu mol\ mol^{-1}$
- Fluctuations barely noticeable in slow responding Instrument F results compared to other instruments.
- Demonstrates the gas measured from the electrolyser met the specified purity of < 1 $\mu mol\ mol^{-1}$





Task 1.3: Trials of rapid response analysis of key contaminants of hydrogen from electrolysis

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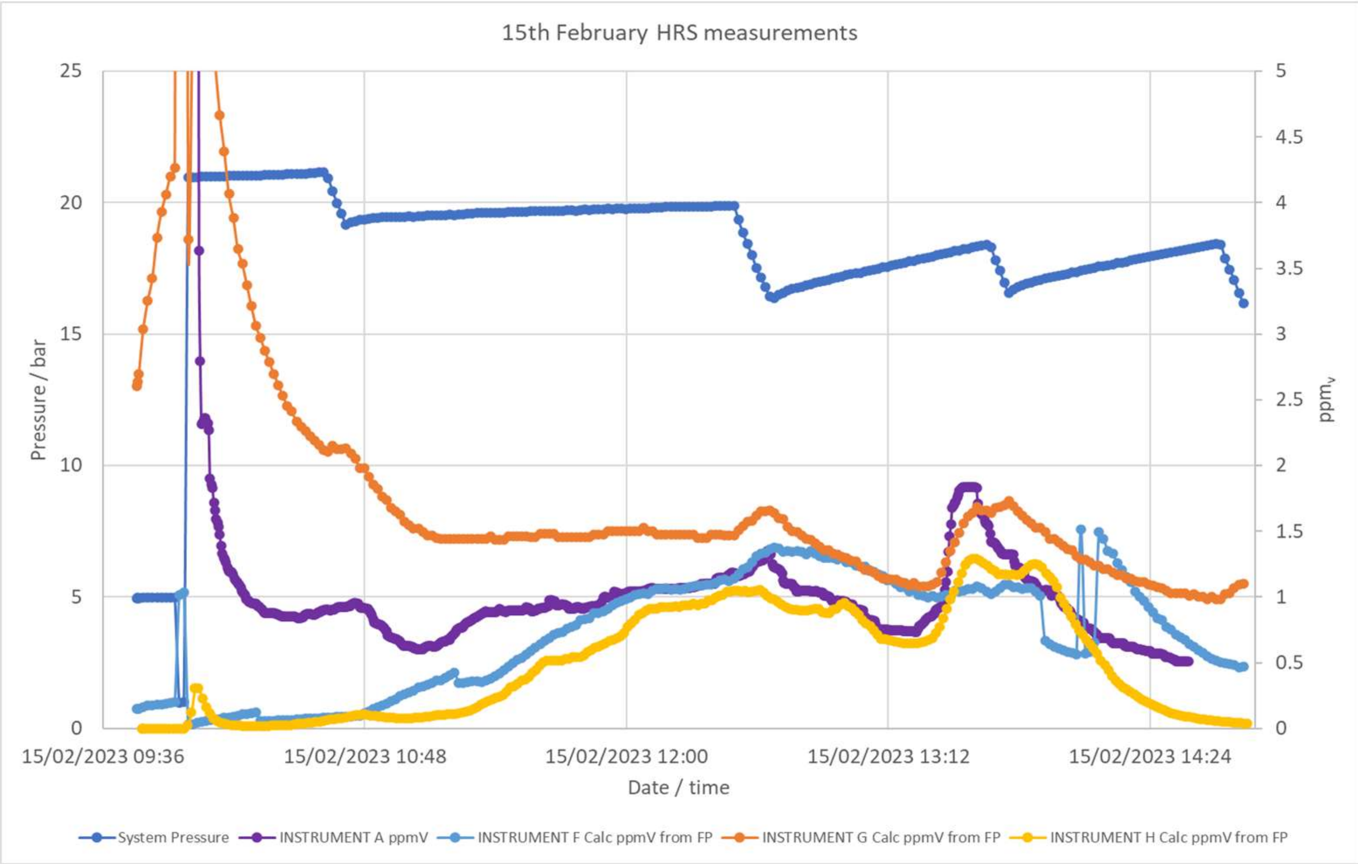
- Additional NPL electrolyser measurements made as part of **Metrology for Hydrogen Vehicles 2** EMPIR project running in parallel to MefHySto with instruments calibrated in MefHySto.
- Measurements made at a Hydrogen refuelling station of hydrogen in the buffer tank at nominally 2 MPa.
- Instrument response time difference demonstrated during surge after 13:00.
- Reasonable agreement in measured value when errors found during NPL calibration corrected for and reference stable.



Work to be completed by project end

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- CEA to perform testing of hydrogen quality produced by electrolysers using water vapour spectrometer validated by PTB and an oxygen analyser loaned by collaborator.

- Testing of loan hygrometers in hydrogen / methane blends (80 % / 20 % , 50 % and 50 % WP5)

- WP1 Reports to be published:

- **D1**: 'Report on the development of new metrology for the measurement of key impurities in hydrogen (including water vapour and oxygen) produced from PEM water electrolysers, with fast response times of a few or tens of seconds'.

- **D2**: 'Report on the testing of online gas analyser instruments for measuring key impurities (including water vapour and oxygen) in hydrogen from electrolysis in situ and during rapidly imposed transient use periods (0–100 %, 200 % peak)'.

MefHySto

Metrology for Advanced Hydrogen Storage Solutions

Thank you! Questions?

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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

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Single cell PEMFC testing with impure gases

MefHySto workshop, Berlin, 3 – 5 Jul 2023

Jonathan Goh, Graham Smith (NPL)

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Contents

- Background
- Impurity Definitions & Impact
- Electrochemical Characterisation with Impure Gases

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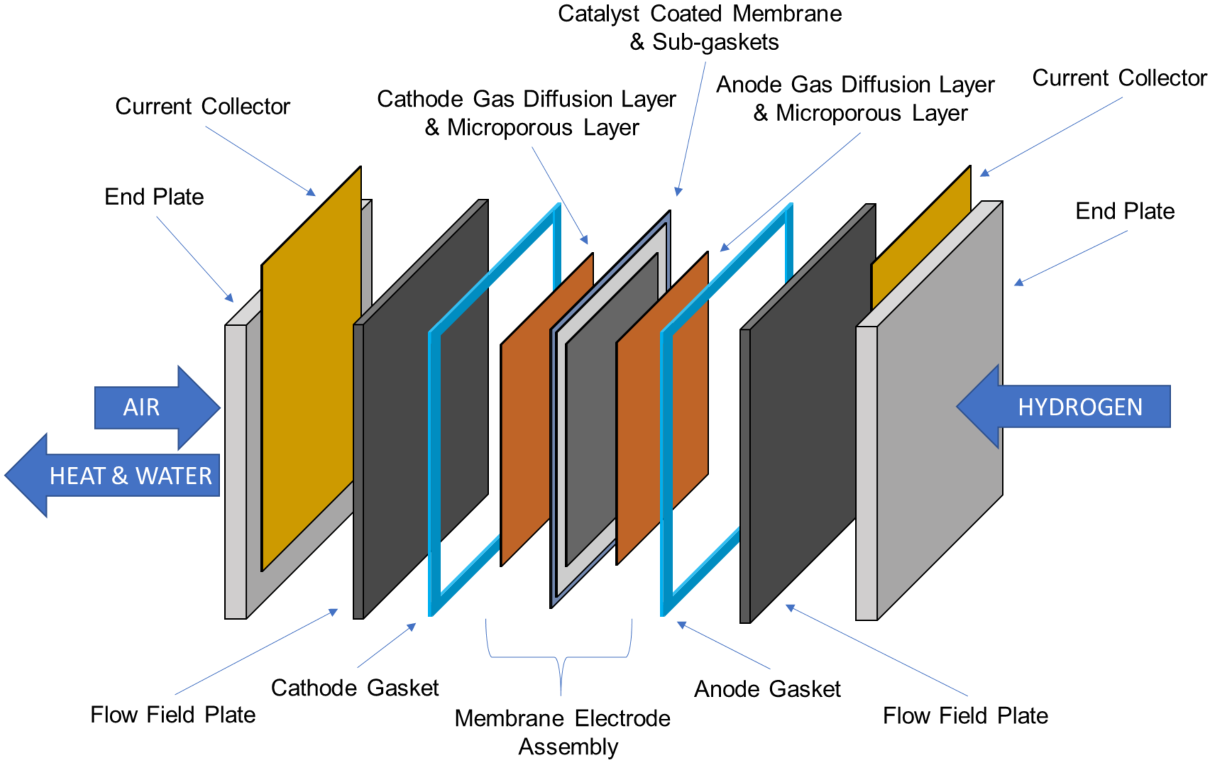
Background

Hydrogen & Fuel Cells

General components with a single cell PEMFC



Polymer electrolyte membrane fuel cell (PEMFC)

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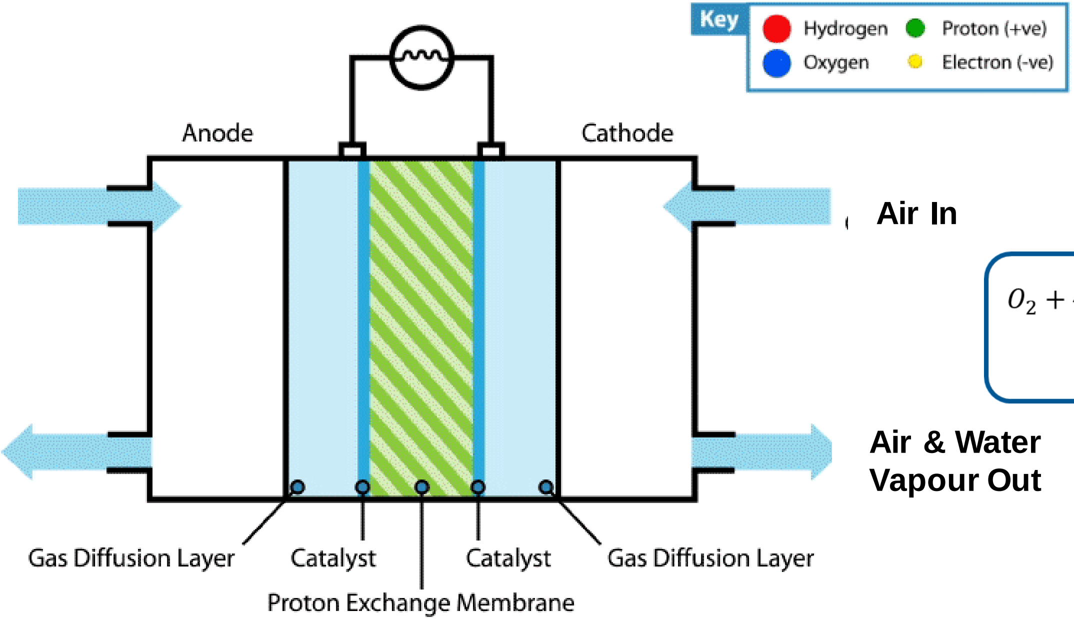
$$H_2 \rightarrow 2H^+ + 2e^-$$

$$E^0 = 0\,V$$



$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$$

$$E^0 = 1.23\,V$$

Image adapted from https://www.intelligent-energy.com/product-support/faqs-your-guide-to-fuel-cells/

Impurity Definitions & Impact

Standards, Scope & Impact

Hydrogen & Air quality

- ISO 14687:2019(D) – hydrogen quality for vehicular applications
  - Contaminant origins from hydrocarbon cracking/gasification
  - *Very little reported about the effect of complex mixtures on fuel cells*
- Challenging to define standard for air quality – type and concentration of contaminant dependent on area
  - Urban – SO_x, NO_x, particulate matter
  - Farm – NH_3
  - High altitude – low O_2 concentration

Composition	Unit	ISO 14687:2019 (D)
Hydrogen	*%*	*99.97*
Water	µmol mol^{-1}	5
NMHC	µmol mol^{-1}	2
Methane	µmol mol^{-1}	100
Oxygen	µmol mol^{-1}	5
Helium	µmol mol^{-1}	300
Nitrogen	µmol mol^{-1}	300
Argon	µmol mol^{-1}	300
Carbon dioxide	µmol mol^{-1}	2
Carbon monoxide	µmol mol^{-1}	0.2
Sulfur compounds	µmol mol^{-1}	0.004
Formaldehyde	µmol mol^{-1}	0.2
Formic acid	µmol mol^{-1}	0.2
Ammonia	µmol mol^{-1}	0.1
Halogenated compounds	µmol mol^{-1}	0.05
Particulates	mg/kg	1

Impact of Impurities on a Fuel Cell

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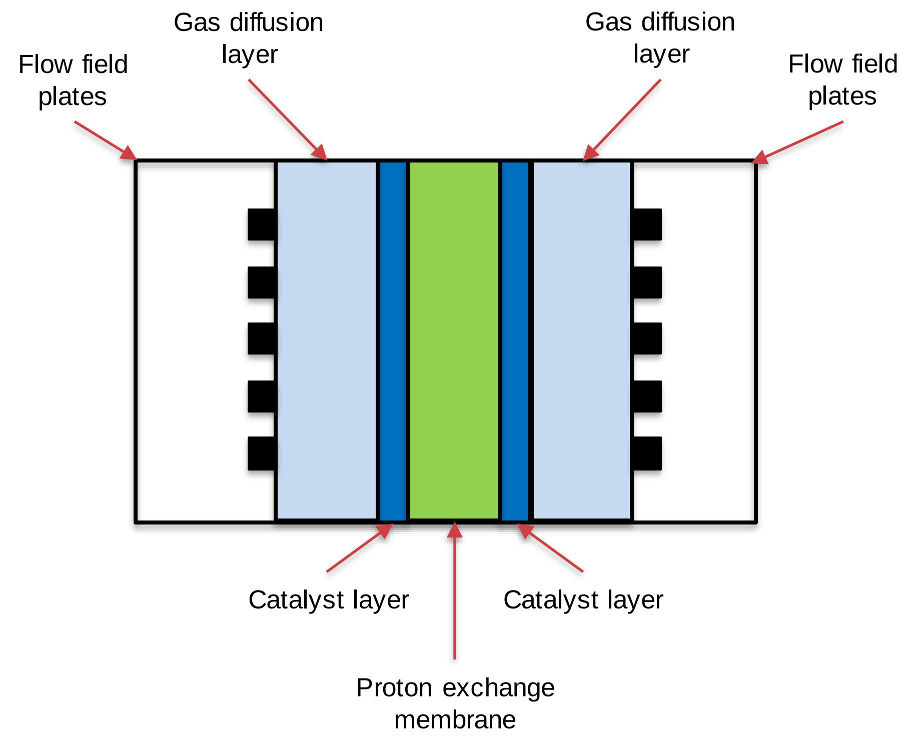
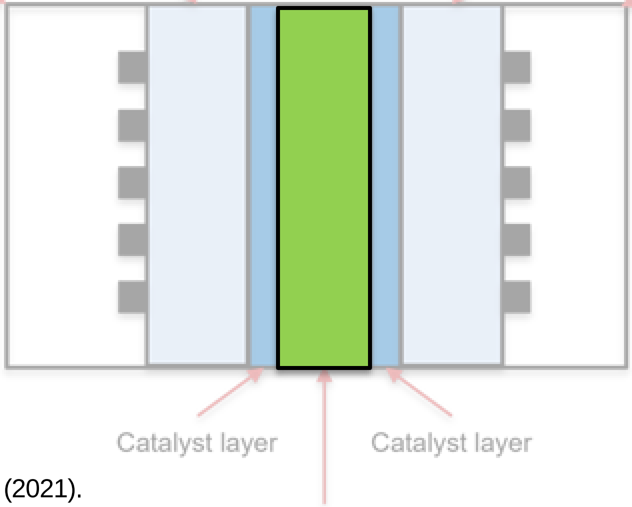
Composition	Unit	ISO 14687:2019 (D)
Hydrogen	*%*	*99.97*
Water	µmol mol^{-1}	5
NMHC (C1 eq.)	µmol mol^{-1}	2
Methane	µmol mol^{-1}	100
Oxygen	µmol mol^{-1}	5
Helium	µmol mol^{-1}	300
Nitrogen	µmol mol^{-1}	300
Argon	µmol mol^{-1}	300
Carbon dioxide	µmol mol^{-1}	2
Carbon monoxide	µmol mol^{-1}	0.2
Sulfur compounds (S1 basis)	µmol mol^{-1}	0.004
Formaldehyde	µmol mol^{-1}	0.2
Formic acid	µmol mol^{-1}	0.2
Ammonia	µmol mol^{-1}	0.1
Halogenated compounds	µmol mol^{-1}	0.05
Particulates	mg/kg	1



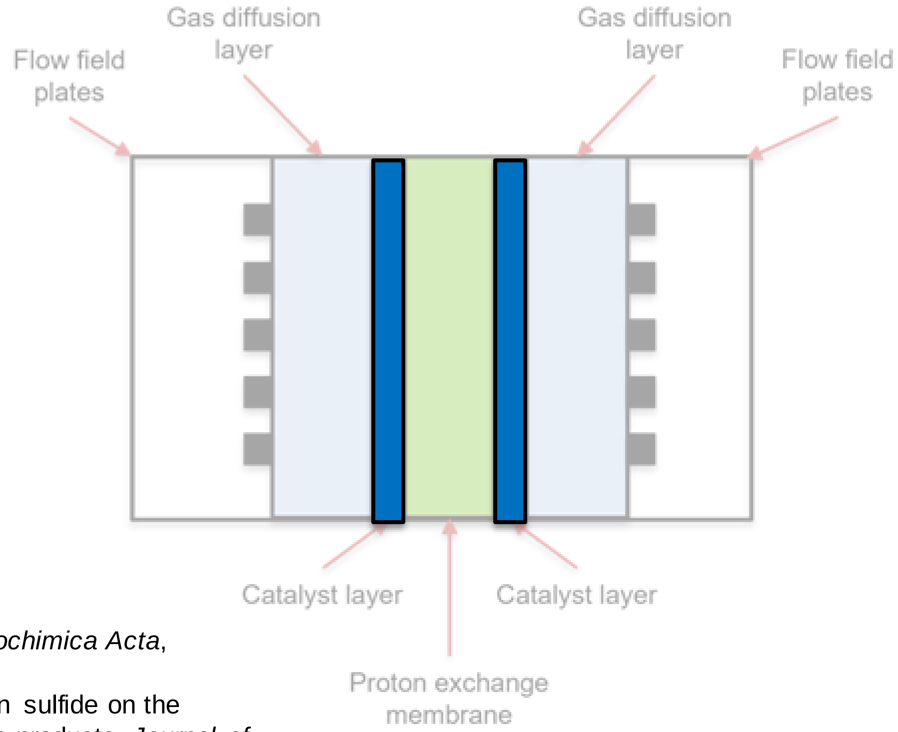
- NH_3 contaminates membrane/ionomer, even at 1 ppm
- Halogens cause membrane dissolution
  - NaCl reduces membrane ionic conductivity
- Fe^{3+} contamination at 1 ppm occupies ion exchange sites on membrane (and active sites on catalyst layer)
  - $Fe^{3+} \rightarrow H_2O_2 \rightarrow$ free radicals
  - Membrane deterioration



1. Schonvogel, D., Büsselmann, J., Schmies, H., Langnickel, H., Wagner, P., & Dyck, A. (2021). High temperature polymer electrolyte membrane fuel cell degradation provoked by ammonia as ambient air contaminant. *Journal of Power Sources*, *502*(May), 229993. https://doi.org/10.1016/j.jpowsour.2021.229993

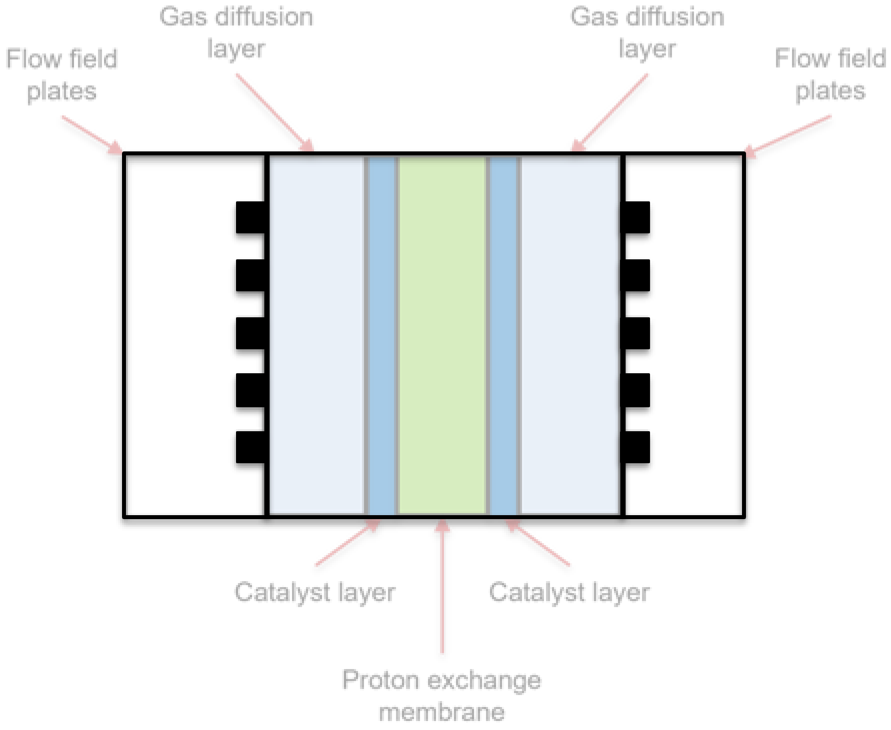
Catalyst poisons

- CO binds with Pt active sites, reversibly
- H_2S severely poisons catalyst, irreversibly
- CO_2 could potentially convert to CO – not widely documented
- CH_2O_2 can cross PEM and contaminate cathode; at 100 ppm may cause coarsening or dissolution of Pt



1. St-Pierre, J. (2010). PEMFC contaminant tolerance limit—CO in H2. *Electrochimica Acta*, *55*(13), 4208–4211. https://doi.org/10.1016/J.ELECTACTA.2010.02.061
2. Lopes, T., Paganin, V. A., & Gonzalez, E. R. (2011). The effects of hydrogen sulfide on the polymer electrolyte membrane fuel cell anode catalyst: H2S-Pt/C interaction products. *Journal of Power Sources*, *196*(15), 6256–6263. https://doi.org/10.1016/j.jpowsour.2011.04.017

- CH_4, CO_2, He, Ar, N_2 etc. dilute hydrogen
  - Effect is more severe with a recirculation loop
  - CO_2 crossover from cathode to anode can lead to high concentrations at the anode



Other effects

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- Tetrachloroethylene and hydrogen chloride cause rapid cell degradation even at 0.05 μmol mol^{-1}
  - Chloride compounds may precipitate and block mass flow
- Particulate matter can clog filters and affect valves
  - Deposition of particles on catalyst layer can cause membrane rupture → short circuits
  - Fe containing particles can cause catalyst/membrane degradation
- Hydrocarbons (except methane) cause varied effects
  - Shorter HCs may act only as diluents
  - Longer HCs may alter wettability of components, poison catalyst or block mass flow
- Oxygen degrades fuel cell
  - Explosion hazard within flammability limit 4 – 94 % concentration (hydrogen in oxygen)
  - May mitigate catalyst poisoning
- Water has no direct impact on fuel cell performance, but
  - May facilitate poisoning by ionic species
  - May alter thermodynamic properties of gases
  - May reduce hydrogen storage capacity a damage storage tanks

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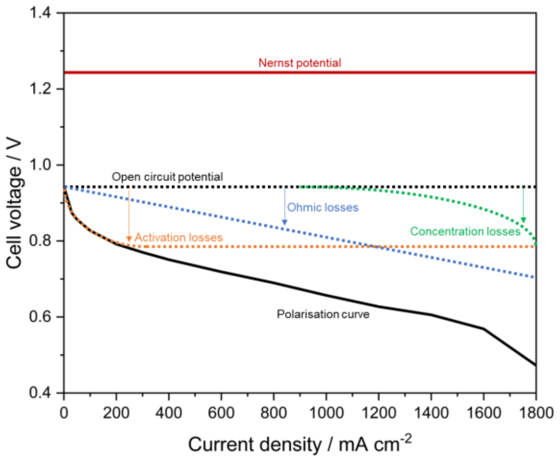
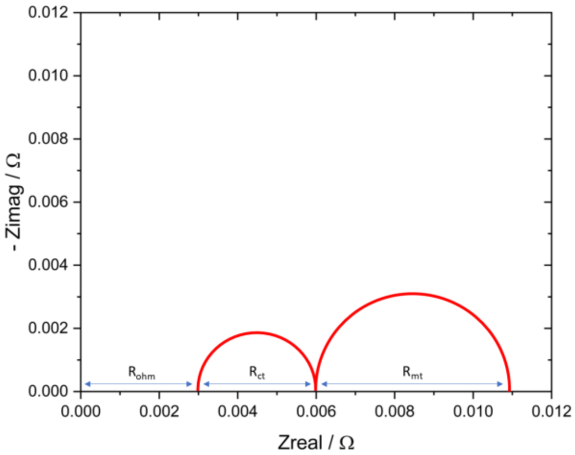
Electrochemical Characterisation

In situ & *In operando* methods

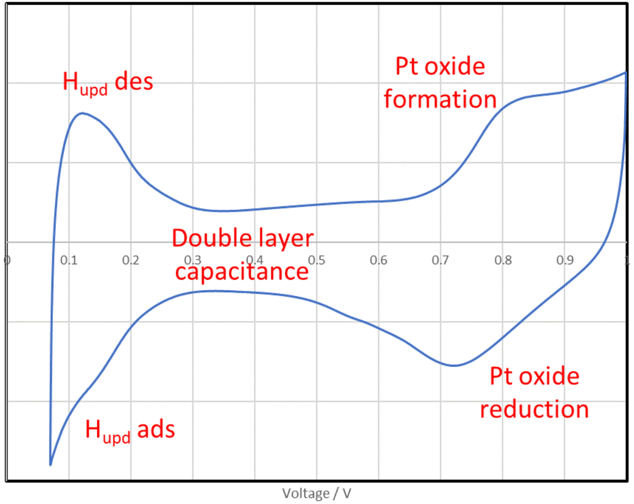
Characterisation methods



Polarisation curve



EIS
(Nyquist plot)



Cyclic
voltammogram

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Thank you!

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