Metrology for Hydrogen Vehicle 2: Any certainty

Thomas Bacquart[1], Marc de Huu[2], Karine Arrhenius[3], Thor Anders Aarhaug[4], Jaana Viitakangas[5], Arul Murugan[1]

[1]NPL, United Kingdom; [2]METAS, Switzerland; [3]RISE, Sweden; [4]SINTEF, Norway; [5]VTT, Finland

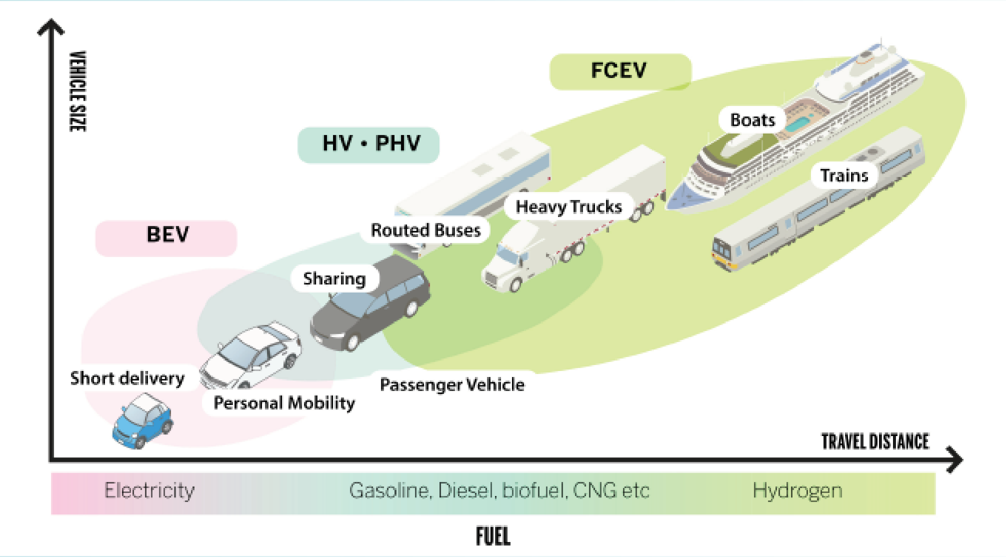
EMN for Energy Gases Workshop – day 2 (22/03/2023) – IPQ Lisbon

This project "Metrology for Hydrogen Vehicles 2" (MetroHyVe 2) has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme under Grant agreement No [19ENG04] .

Hydrogen momentum

“Climate neutral” Europe: the overarching objective of the European Green Deal. The EU aims to reach net-zero greenhouse gas emissions by 2050.

Number of FCEV in Europe by 2030: **1 million**
FC durability: **7000 hours FCEV / 30000 hours heavy duty FCEV**



FCEV provide the following benefits:

No emission

Distance range very similar to conventional petrol vehicles (trucks, fork lift, passenger vehicles, train)

Truck fleet in Switzerland
(> 1600 trucks by 2025)

Fuel cell bus
(> 600 by 2023)

Hydrogen trains
(54 in Europe by 2022)

Hydrogen infrastructure
Refuelling station (HRS)

- Supplied at 35 or 70 MPa
- Different applications (heavy-duty, passenger, small vehicles)
- 5 - 50 kg per fill (full tank)
- 3 - 10 minutes to fill

HRS available in 2021
(> 137 HRSs in Europe)

Planned HRSs (i.e. under construction)

Hydrogen fuel Deployment phase

Measurement is important

METROLOGY for HYDROGEN VEHICLES 2

Hydrogen quality at the nozzle
(**sampling** & **analysis**)

Image: Example of hydrogen refuelling, not related to presentation

Onsite production
+
Water sensor

Impact to vehicle

Measurement is important

Hydrogen quality at the nozzle
(**sampling** & **analysis**)

Onsite production
+
Water sensor

Issue with water amount fraction

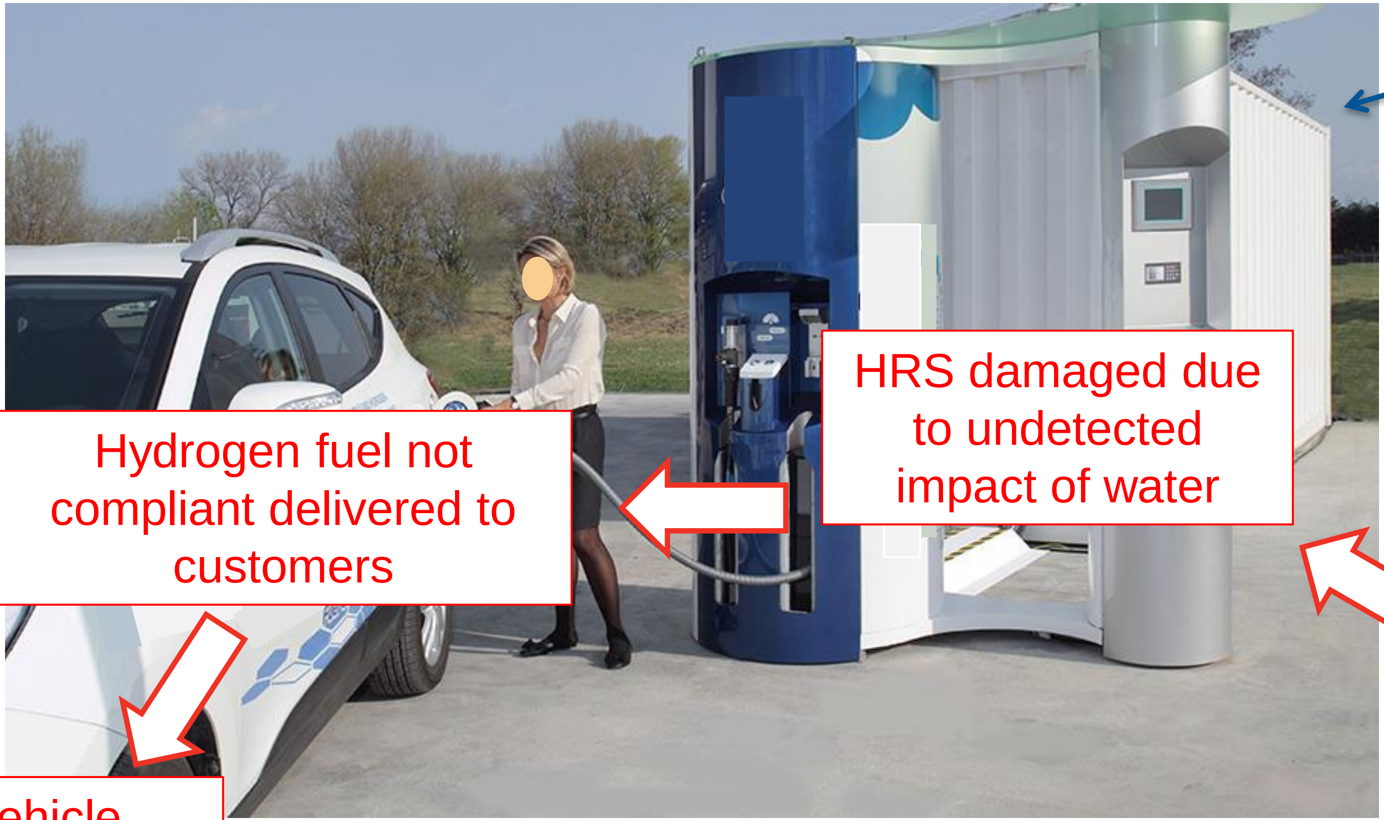
+

Sensor not calibrated / failed

Impact to vehicle

Measurement is important

METROLOGY for HYDROGEN VEHICLES 2



Hydrogen fuel not compliant delivered to customers

HRS damaged due to undetected impact of water

Impact on vehicle performance and lifetime

Onsite production

+

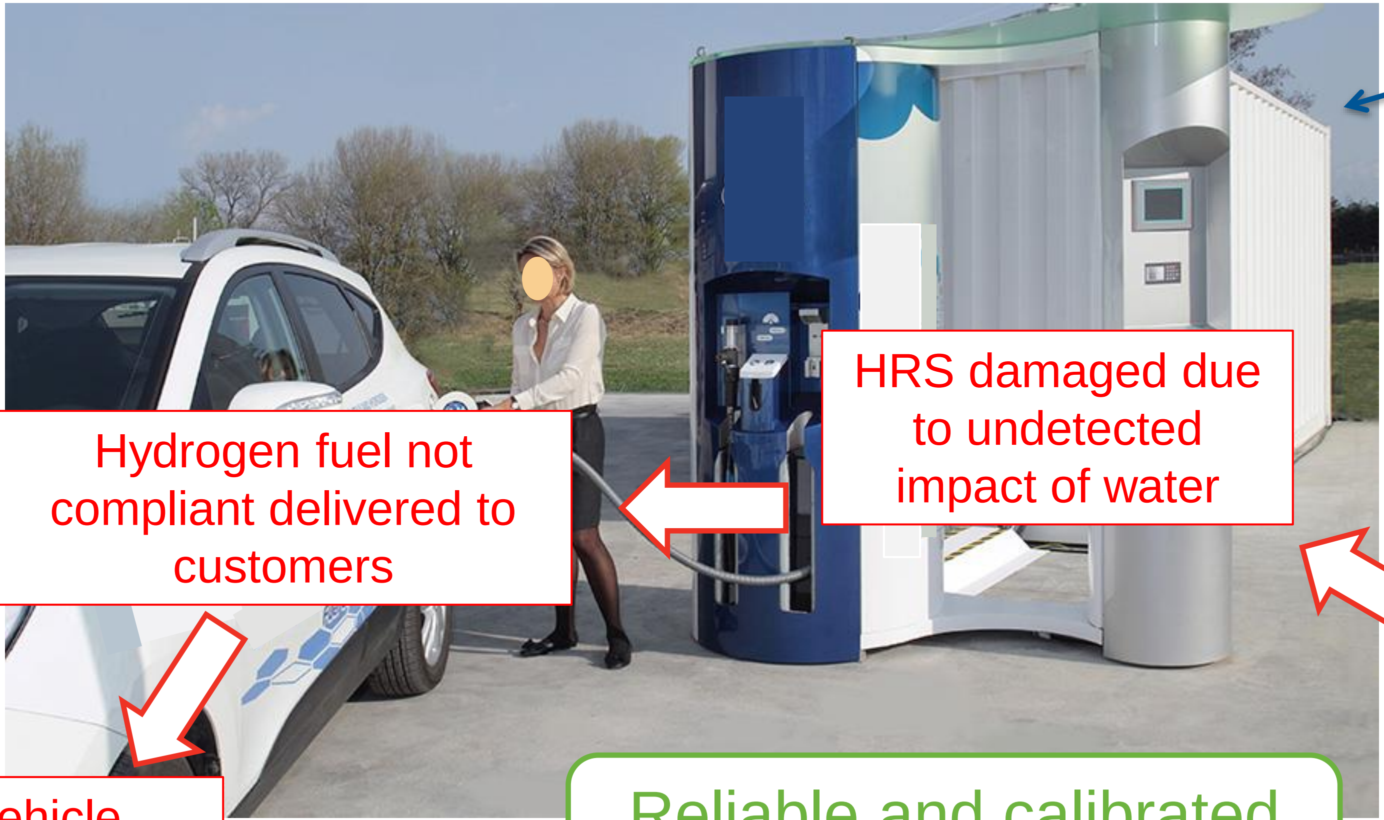
Water sensor

Issue with water amount fraction

+

Sensor not calibrated / failed

Measurement is important



Onsite production

+

Water sensor

Calibration - reliability

Issue with water amount fraction

+

Sensor not calibrated / failed

HRS damaged due to undetected impact of water

Hydrogen fuel not compliant delivered to customers

Impact on vehicle performance and lifetime

Reliable and calibrated measurement is key

Five Metrology Challenges for the Hydrogen Industry

METROLOGY for HYDROGEN VEHICLES 2

Hydrogen quality at the nozzle
(**sampling** & **analysis**)
Regulation - ISO 14687

Quality control
Reliability – ISO19880-8

Contaminant impacting fuel cell
Reliability

Accurate billing – **flow metering**
Consumer – OIML R139

Objectives

Solve the measurement challenges

Flow metering

Enable accurate and equivalent measurement of hydrogen dispensed to vehicles (light duty and heavy duty) to cost the customer correctly

OIML R139-1

Hydrogen quality control

Ensure purity analysis can be carried out accurately offline and online to provide reliable results prevent degradation of fuel cell systems

ISO 14687 / ISO 21087 / ISO 19880-8

Sampling

Support refuelling stations in taking representative samples of hydrogen for testing and ensuring worldwide equivalence

ISO 19880-9

Fuel cell testing

Support fuel cell stack testing standardisation, improve reproducibility for automotive stack testing (industry benchmarking), support developing the future fuel cell tech

IEC/TC 105

Challenge 2 – Quality control

METROLOGY for HYDROGEN VEHICLES 2

DIRECTIVE 2014/94/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 22 October 2014 on the deployment of alternative fuels infrastructure:

“The hydrogen purity dispensed by hydrogen refuelling points shall comply with the technical specifications included in the EN17124 standard.”

	ISO 14687:2019 / EN 17124:2022	
	Max. admissible value [µmol/mol]	notes
Water	5	
Total hydrocarbons (TC)	2 except CH_4	including oxygenated organic species
Methane	100	
Oxygen	5	
Helium	300	
Nitrogen	300	
Argon	300	
carbon dioxide	2	
Total sulphur compounds	0.004	H2S, COS, CS2, mercaptans (NG)
Carbon monoxide	0.2	Total of these compounds not to exceed 0.2 µmol/mol
Formaldehyde	0.2	
Formic acid	0.2	
Ammonia	0.1	
Halogenated compounds	0.05	HCl, organic R-Cl
Max. particulate conc.	1 mg/kg	

Measurement system
(analytical laboratory / online analyser)

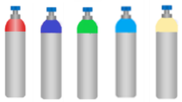
Trust
- Accreditation
- Technical evidence

Reliability
- Accurate measurement
- Traceability and uncertainty

MetroHyVe 2 – Novel reference materials study

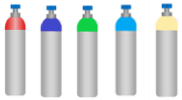
METROLOGY for HYDROGEN VEHICLES 2

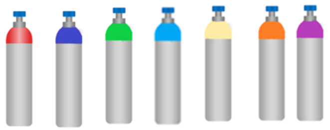
Component	Sub-set 1 – Compounds in violation	Sub-set 2 - ‘most challenging	Sub-set 3 - ISO 14687/EN17124 – full scope	Additional comments
	Amount fraction (µmol/mol)			
Nitrogen	300	(300) Not measured	300	
Helium	-	-	300	
Argon	-	-	300	
Carbon monoxide	-	-	0.2	
Carbon dioxide	2	-	2	
Methane	-	-	100	
tot NMHC	Propane: 0.7 µmol/mol	n-butane and Ethanol	Ethane: 1 µmol/mol	Equivalent to 2 µmol/mol CH_4
Oxygen	5	5	5	
Water	5	-	5	
Ammonia	-	0.05 - 0.3	0.05 - 0.3	
Formaldehyde	-	0.05 - 0.3	0.05 - 0.3	
Formic acid	-	0.05 - 0.3	0.05 - 0.3	
tot halogenated	$C_4Cl_4F_6$: 0.012	C_2Cl_4: 0.012	Cl_2CH_2: 0.025	Equivalent to 0.05 µmol/mol Cl basis
tot sulphur	H_2S: 0.003 - 0.007	C_2H_6S: 0.003 - 0.007	COS: 0.003 - 0.007	Equivalent to 0.004 – 0.010 µmol/mol Sulphur basis
Hydrogen	Balance	Balance	balance	



5 types of cylinder

5 types of cylinder

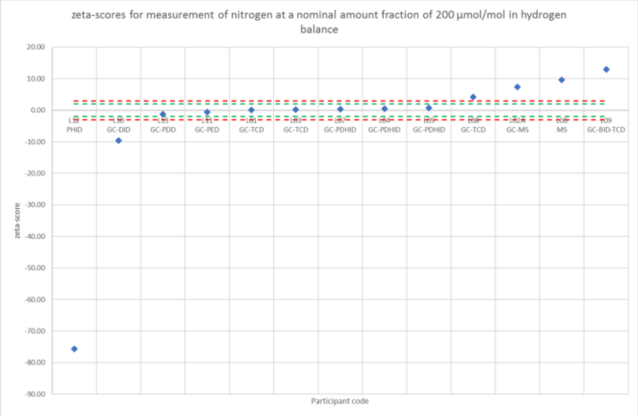




7 types of cylinder

1 year stability

Evolution of intercomparison



METROLOGY for HYDROGEN VEHICLES 2

2017

EURAMET

EURAMET 1220

2 compounds (CO / H_2S in H_2)

10 participants

2 cylinder circulated

2 years

2019

METROLOGY for HYDROGEN VEHICLES

16ENG01 MetroHyVe

4 compounds (CO, N_2, H_2O in H_2 / H_2S in H_2)

13 participants

20 cylinders

1 year

2021

CCQM K164

8 compounds (He, Ar, N_2, CO_2, CH_4, C_2H_6, CO, C_2H_6S)

9 participants

9 cylinders

1 year

2022

METROLOGY for HYDROGEN VEHICLES 2

19ENG04 MetroHyVe 2

8 compounds (N_2, CO_2, CH_4, C_3H_8, CO, H_2S, $C_4Cl_4F_6$, O_2, H_2O)

12 participants

12 cylinders

6 months

2022-2024

HyQUALITY H_2 EUROPE

HyQuality

Hydrogen Europe

Benefit from EMPIR Metrohyve 1&2 project

→ Large scale hydrogen fuel analysis / analytical laboratories

Online analysis at hydrogen refuelling stations

METROLOGY for HYDROGEN VEHICLES 2

MetroHyVe 1
- Validation of online analyser in laboratory

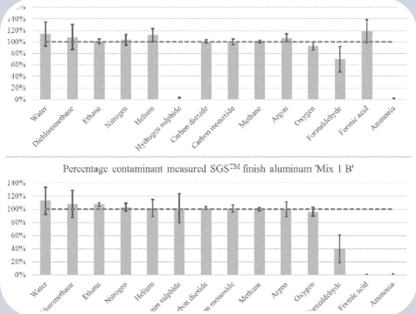
MetroHyVe 2
- Evaluation of sensor performance in laboratory

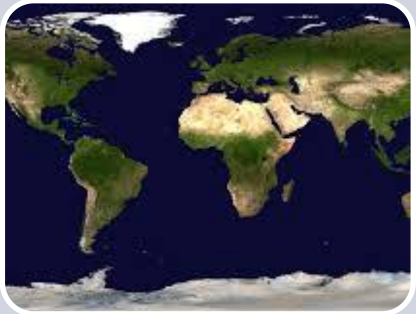
MefHySTO
- Evaluation of H_2O sensor performance in laboratory

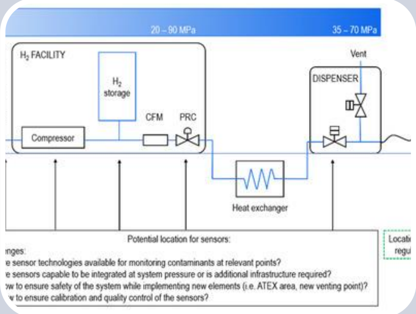
MetroHyVe 2: Implementation at hydrogen refuelling stations
- Performance of instruments (sensor, online analyser)
  - ATEX GC analyser, FTIR, microGC,
  - IMR-MS, GC-PED, OFCEAS, CRDS
- Environment (ATEX zone, outside zone)
- Calibration requirements
- Risk assessment

Achievements

Hydrogen quality control







New Primary Reference Materials stability study for reactive compounds (ammonia and formaldehyde) in hydrogen

Multi-contaminants gas mixture in hydrogen

3 subset (21 impurities) in 7 different cylinders

similar to 140 stability study ongoing

Setting up most complex offline laboratory comparisons open to all laboratories worldwide

12 participants - 8 compounds including reactive

Study of sensor performance for water in hydrogen in laboratory condition

Results reported to manufacturer to support R&D and applications

First peer review on challenge for sensor development in hydrogen and implementation at HRS

https://www.sintef.no/projectweb/metrohyve-2/

Arrhenius, et al. (2022)
https://doi.org/10.3390/pr10010020

Challenge 3 - Sampling

METROLOGY for HYDROGEN VEHICLES 2

Hydrogen refuelling station

Hydrogen purity laboratory

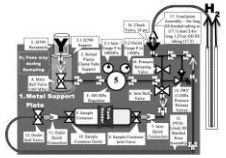
Measurement is only as good as the sample

Challenge 3 – Sampling

Hydrogen refuelling station

Japan

H2 qualitizer



ASTM D7606

HySam

Spot sampling

Hydrogen sample

study of all sampling cylinder used in the industry for reactive compounds

Hydrogen purity laboratory

Sampling bilateral comparison

Support standardisation ISO TC197 WG33 – hydrogen fuel sampling at HRS nozzle

Challenge 3 - Sampling

Sampling intercomparison

- 1 hydrogen refuelling station for research purpose
- 4 devices (ENGIE, Air Liquide, HySam, H2 Qualitizer)
- As close as possible to repeatability condition

Analysis

- Repeatability condition
- Offline at NPL and online by ENGIE

Challenges

- Integration of station parameters (i.e., temperature, filling rate)
- System more complex than expected (i.e., storage bank)
- How to verify sampling methodology with representative and reliable system?

Particulate sampling

Particulate sampling challenges

- Low mass: 1 mg/kg
- Conditions: flow up to 60 g/s, pressure up to 700 bar
- Lack of harmonisation on filter type, validation

Filter (particulate penetration)

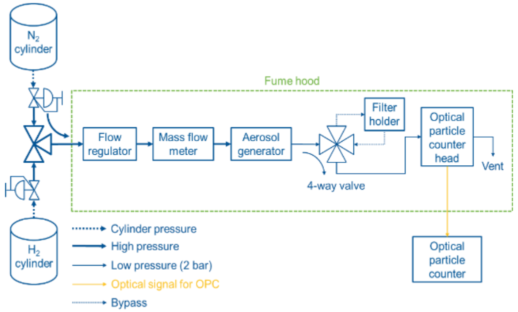
- Particulate penetration on 0.2 and 5 µm filter
- Experiment at low pressure (few bar) in hydrogen matrix
- No 300 nm particulate penetration on 0.2 and 5 µm filter

Repeatability

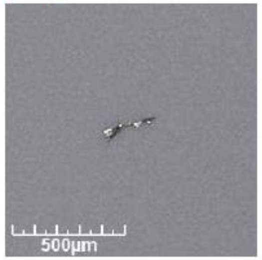
- Repeatability of particulate sampling at hydrogen refuelling station
- Investigation of particulate by microscopy (size, type)

Further works

- How to calibrate particulate measurement at HRS conditions (i.e., pressure)
- Online particulate measurements
- Better understanding of particulate at HRS



Particles:



Achievements

Sampling

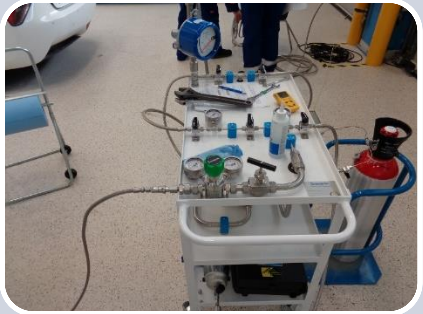
Peer review article on hydrogen sampling at hydrogen refuelling stations including state of the art instrumentation and cylinder

1st repeatability study of particle sampling device (HyDAC)

Evaluation of 5 types of filter performance including penetration test with reference particles in H2

1st bilateral comparison of ASTM and EU approach on sampling (joint activity between CDFA and SINTEF in California) - 2 bilateral sampling and analysis

Tested sorbent tubes at high pressure for capturing and transporting very low level reactive impurities



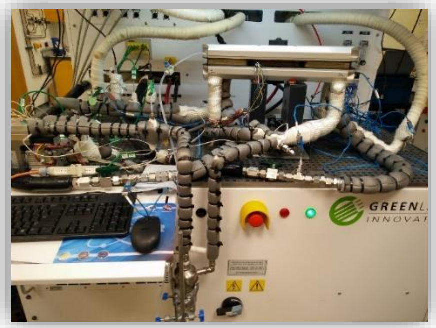
1st metrological contamination of hydrogen gas into fuel cell hydrogen vehicle and sampling from the vehicle in order to demonstrate accurate sampling

Arrhenius et al. (2021)
https://doi.org/10.1016/j.ijhydene.2021.08.043

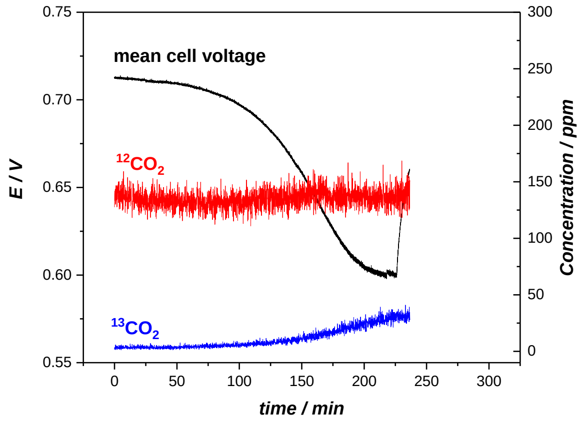
https://www.sintef.no/projectweb/metrohyve-2/

Challenge 4 – MetroHyVe 2 - Fuel cell stack testing

METROLOGY for HYDROGEN VEHICLES 2



Fuel cell stack with recirculation loop



Fuel cell stack experiment

- No harmonised methodology to study contaminants impact on fuel cell stack
- Study of contaminant impact to fuel cell stack with recirculation are not reproducible
- Revision of ISO 14687 based on study not representative of FCEV

Reactive gases

•Water	5 µmol/mol
•Oxygen	5 µmol/mol
•Carbon dioxide	2 µmol/mol
•Total hydrocarbon compounds	2 µmol/mol
•Formic acid	0.2 µmol/mol
•Carbon monoxide	0.2 µmol/mol
•Formaldehyde	0.2 µmol/mol
•Ammonia	0.1 µmol/mol
•Halogenated compounds	50 nmol/mol
•Total sulphur compounds	4 nmol/mol

Inert gases

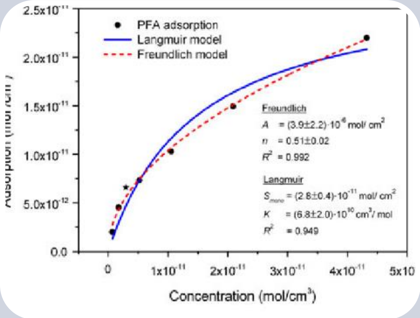
•Helium	300 µmol/mol
•Nitrogen	300 µmol/mol
•Argon	300 µmol/mol

Non-gases

•Particulates	1 mg/kg

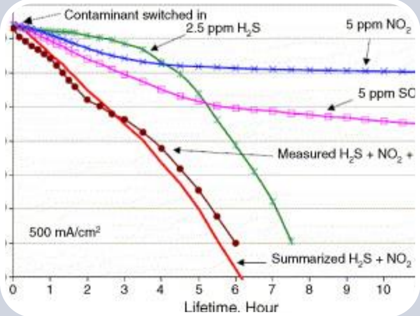
Achievements
Fuel cell testing

4 different and representative fuel cell stacks provided by 3 different manufacturers to the project consortium



Start of adsorption and desorption study of reactive compounds (ammonia) in hydrogen fuel cell system in correlation with online measurement by FTIR

Review of fuel cell testing system and differences between test benches



New literature review on reactive contaminant relevant for fuel cell impurity testing

Start of clean-up study of fuel cell pipes after exposure to contaminant (inert, hydrocarbons, reactive species) in hydrogen

https://www.sintef.no/projectweb/metrohyve-2/

Next steps

METROLOGY for HYDROGEN VEHICLES 2

MetroHyVe 2 achievements

How to impact

	MetroHyVe 2 achievements	How to impact
Quality control	• New binary and multi-compounds reference materials • Interlaboratory comparison scheme • Sensor testing • Good practice guide for online analysis at hydrogen refuelling stations	• Application by analytical laboratory • Support routine laboratory • Development of sensor testing facility • Extensive online analysis campaign at hydrogen refuelling stations (HyQUALITY H_2 EUROPE)
Sampling	• Guideline for sampling cylinder based on performance • 1st sampling methodology intercomparison • Improved good practice guide for particulate sampling • New sampling methodologies • Support to ISO TC197 WG33	• Development of metrological facility for sampling validation (gas & particulate) • Evaluation of new material passivation • New particulate analysis development • Heavy duty sampling
Fuel cell stack testing	• New stack testing methodology • Better understanding of bench and test parameters impact on results • Improved reproducibility	• Application of new results to support redefinition of ISO14687 threshold • Development of fuel cell metrology

New metrology infrastructure required
Applied metrology / deployment of findings
More joined activities with industry

Topic strategy between programs

Hydrogen Europe™ METROLOGY PARTNERSHIP EURAMET

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Thank you, any questions

Interested in the project, don't contact Thomas Bacquart (NPL coordinator) / Thor Aarhaug (Impact leader)
Website: https://www.sintef.no/projectweb/metrohyve-2/