

How clean is your hydrogen? An overview of metrological developments underpinning hydrogen-fuel quality assurance

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National Physical Laboratory (UK)

National Physical Laboratory



“The National Physical Laboratory (NPL) is the UK's National Metrology Institute, and is a world-leading centre of excellence in developing and applying the most accurate measurement standards, science and technology available.”

Hydrogen quality



Production / distribution

- Optimisation
- Performance / maintenance
- Cost of production

Legal requirements for H₂ Supplier

- Alternative fuel infrastructure directive (AFID)
- ISO14687:2019
- EN17124:2022
- SAE J2719:202003



Customer / End users

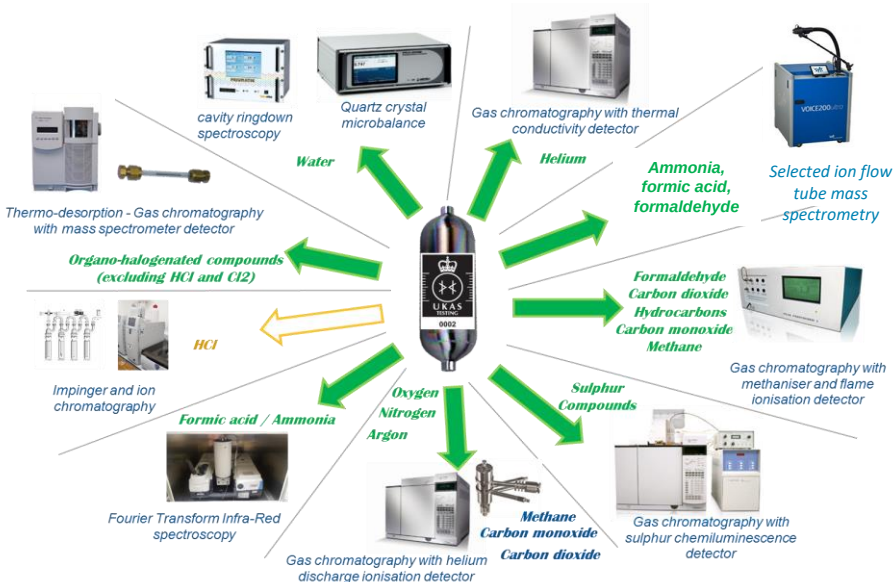
- Reliability of vehicles
 - FCEV (> 5000h)
 - HGV (> 10000h)
- No incidents / loss of power
- Fair fuel price

Hydrogen quality standards: ISO 14687 / EN 17124

	ISO 14687:2019 / EN 17124:2022	
	Max. admissible value [μmol/mol]	notes
Water	5	
Total hydrocarbons (TC)	2	Exclude methane; including oxygenated organic species
Methane	100	
Oxygen	5	
Helium	300	
Nitrogen	300	
Argon	300	
carbon dioxide	2	
Total sulphur compounds	0.004	H ₂ S, COS, CS ₂ , 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	

Multiple compounds / large range of amount fraction
Reactive compounds / extremely low amount fraction

NPL's Hydrogen Purity Laboratory

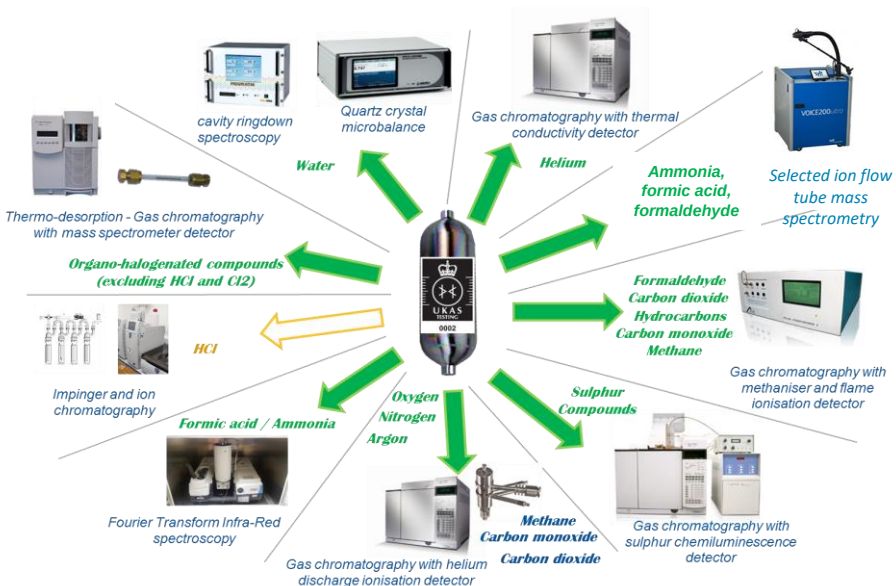


Gas analysis	ISO/FDIS 14687	Analytical Method	Detection Limit	ISO 17025	Required amount of gas
	[$\mu\text{mol/mol}$]		[$\mu\text{mol/mol}$]		[L]
Water	5	QCM CRDS	0.2 0.030	Yes	30 30 - 60
Total Hydrocarbons	2	GC-Methaniser-FID	0.05	Yes	2
Methane	100	GC-Methaniser-FID	0.05	Yes	2
Oxygen	5	GC-PDHID	0.3	Yes	2
Helium	300	GC-TCD	10	Yes	2
Argon	300	GC-PDHID	0.3 1	Yes	2
Nitrogen	2	GC-Methaniser-FID	0.02	Yes	2
Carbon Dioxide	0.2	GC-Methaniser-FID	0.02	Yes	2
Carbon Monoxide	0.004	GC-SCD	0.001	Yes	1
Total sulphur	0.2	GC-Methaniser-FID SIFT-MS	0.05 0.02	No	2 2
Formaldehyde	0.2	FTIR SIFT-MS	0.05 0.02	No	30 2
Formic Acid	0.1	FTIR SIFT-MS	0.05 0.02	No	30 2
Ammonia	0.05	TD-GC-MS	0.016	No	1.5
Key halogenated compounds					
Sampling		Sampling tool	Hardware	Expertise	
Gas sampling		H2 Qualitizer	Yes	> 50 samplings	
Particulate sampling	1 mg/kg	HYDAC H70	Yes	> 10 samplings	



Particulate and gas sampling at 35/70 MPa

NPL's Hydrogen Purity Laboratory



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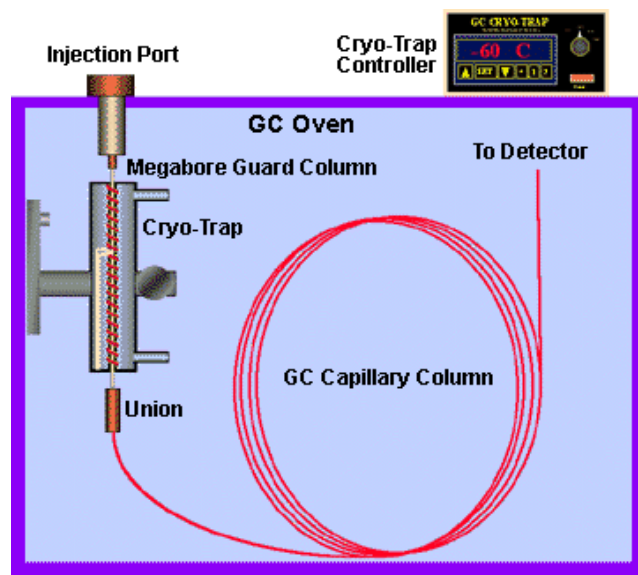
Particulate and gas sampling at 35/70 MPa

Total sulphur analysis at ultra trace level

Cryo-focussing GC-SCD

Analytical methods:

- Gas chromatography with sulphur chemiluminescence detector (GC-SCD)
- Preconcentration step: on column cryofocussing
- Non retaining column
- Sulphur selective detector



Achievements:

- Linearity: 0.12 – 16 nmol/mol
- Repeatability 5.1%
- Intermediate precision: 9.3%
- Relative uncertainty ($k=2$): 21%
- Trueness
 - Verified against NPL PRMs
 - OCS (349 picomol/mol) / DMS (488 picomol/mol)

OCS amount fraction with expanded uncertainty ($k=2$) [pmol/mol]	H ₂ S amount fraction with expanded uncertainty ($k=2$) [pmol/mol]	DMS amount fraction with expanded uncertainty ($k=2$) [pmol/mol]	Matrix
14918 ± 190	n.p.	n.p.	H ₂
5986 ± 84	n.p.	n.p.	H ₂
349 ± 11	n.p.	n.p.	H ₂
n.p.	15135 ± 130	n.p.	H ₂
n.p.	n.p.	15795 ± 320	H ₂
n.p.	n.p.	801 ± 18	H ₂
n.p.	n.p.	208600 ± 4200	H ₂
n.p.	n.p.	488 ± 10	H ₂
n.p.	6830 ± 70	n.p.	H ₂

Total sulphur analysis at ultra trace level

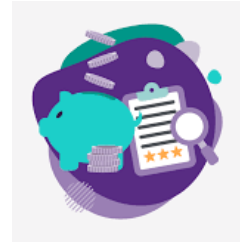
Cryo-focussing GC-SCD – analytical campaign

Hydrogen refuelling station	Total sulphur amount fraction with uncertainty ($k=2$) [nmol/mol]	Feedstock
HRS 1	< 0.16	Electrolysis
HRS 2	< 0.16	steam reformer / natural gas
HRS 3	< 0.16	
HRS 4	< 0.16	
HRS 5	0.29 ± 0.12	SMR
HRS 6	0.26 ± 0.12	Electrolyser
HRS 7	0.19 ± 0.08	WE
HRS 8	< 0.16	WE
HRS 9	< 0.16	SMR/BIO
HRS 10	0.20 ± 0.08	SMR/BIO
HRS 11	< 0.16	n/a

- New measurement method – peer review article drafted (expect publication in summer 2022)
- Better resolution for total sulphur analysis in hydrogen fuel
- Important to understand sulphur presence and behaviour in hydrogen

Hydrogen quality – how to know?

- Internal capability or outsourcing?
- Analytical laboratories in Europe - Increasing availability
 - Air Liquide, Linde, ENGIE, ENAGAS...
 - ZSW, ZBT, DLR, CNH2...
 - Intertek, SGS, DNV...
- No standardised methodology in Europe
 - Various analytical methods,
 - working range,
 - limit of detection,
 - volume of gas



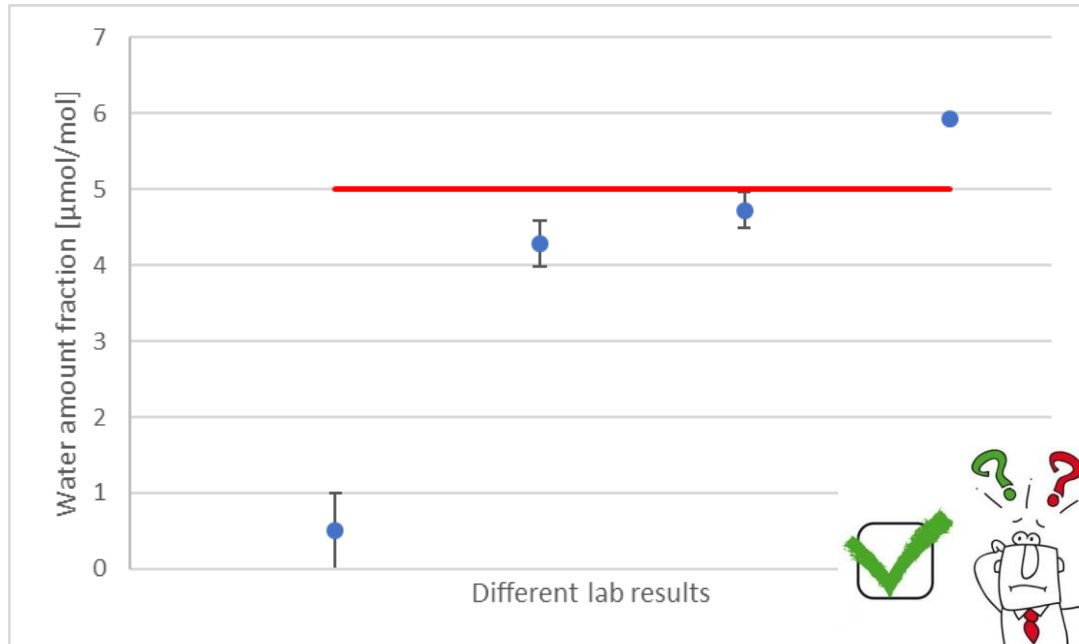
23rd of Sept 2021
Final Public Event
A platform to discuss
'DROGEN QUALITY for PEMFCs

<https://hydraite.eu/>

Beurey et al. 2021 - Review and Survey of Methods for Analysis of Impurities in Hydrogen for Fuel Cell Vehicles According to ISO 14687:2019 (<https://doi.org/10.3389/fenrg.2020.615149>)

Hydrogen quality analysis - How to benchmark laboratory?

Results of different laboratories

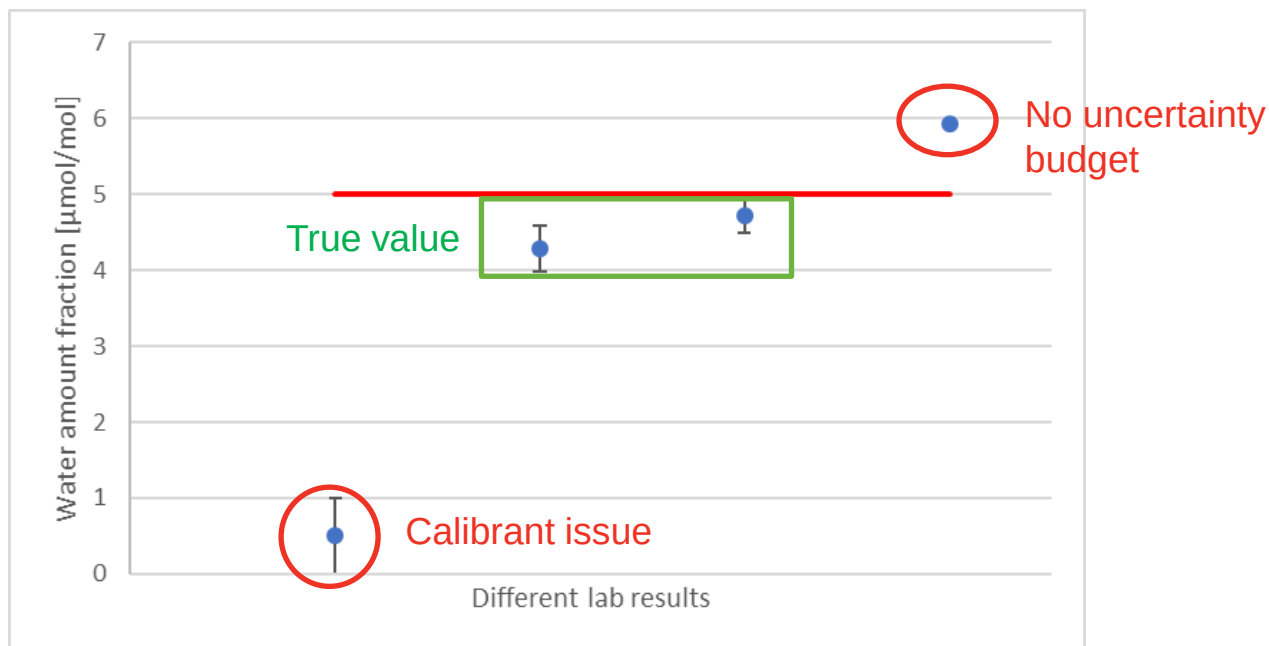


Laboratories, results....

How to benchmark laboratory?

Where is the true value?

Results of different laboratories

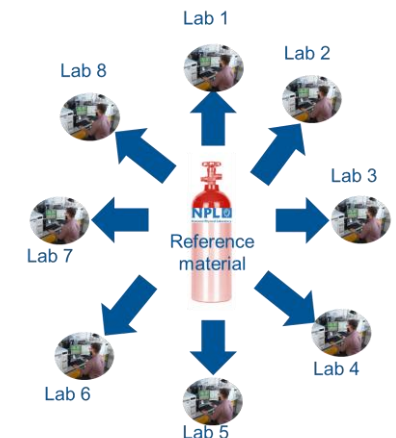


How to evaluate laboratory performance before contracting or to new customer?

- Certified reference materials
- Inter-laboratory comparison



Commercially available
(National metrology
institute, gas supplier)



Importance of comparability and intercomparisons

Accreditation

- Requirements for ISO 17025 and/or ISO 21087
- Technical evidence



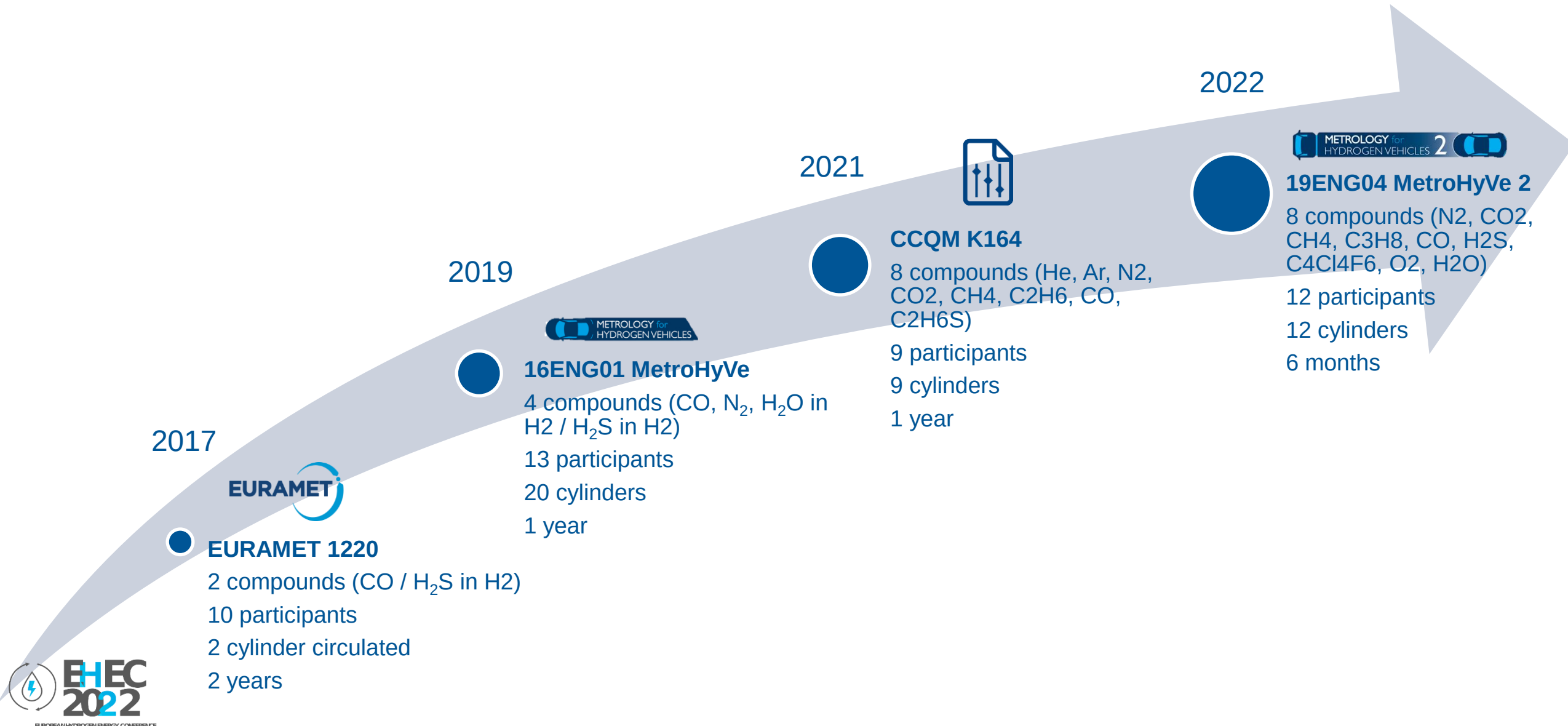
International
Organization for
Standardization

Reliability

- Incorrect measurement consequences:
 - False negative: poor performance of vehicle
 - False positive: unnecessary investigation of HRS



Evolution of intercomparison



MetroHyVe 2 – Novel reference materials study

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 ₄ Cl ₄ F ₆ : 0.012	C ₂ Cl ₄ : 0.012	Cl ₂ CH ₂ : 0.025	Equivalent to 0.05 μmol/mol Cl basis
tot sulphur	H ₂ S: 0.003 - 0.007	DMS: 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

EMPIR Metrology for Hydrogen Vehicles 2

Facts:

- 18 European partners including NMIs and industry
- Coordinator: NPL
- Project budget: 2.3M€
- Length: 36 months
- Timeline: Aug 2020 – July 2023

WP1: Flow metering Leader: METAS (CH)

- Heavy duty primary standards
- Secondary standards



Flow metering METAS

WP 2: Quality control Leader: RISE (SE)

- New reference material
- Inter-laboratory comparison
- Sensors and analyser at HRS



Quality control RISE

WP5: Impact Leader: SINTEF (NO)

- Support standardisation
- Training and workshop
- Stakeholder engagement



Creating impact SINTEF

WP3: Sampling Leader: NPL (UK)

- Cylinder passivation
- Sampling inter comparison (EU/US/JP)
- Particulate sampling
- New sampling methodology



Sampling NPL

WP4: Fuel cell stack Leader: VTT (FI)

- Definition of critical testing parameter
- Reproducibility testing
- Stack with recirculation test protocol



Fuel cell stack VTT

Get involved:
Stakeholders, collaborators

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

Futures and perspectives

- Growth of commercial laboratory availability
 - Need to provide competence evidences
 - Equivalence with benchmark laboratories
- Importance of intercomparison – reliability of results
 - Maturity of interlaboratory comparison
 - Reference gas cylinder (multi components in hydrogen)
- Importance of availability of appropriate methods and in-depth measurements methods
 - New total sulphur method
 - Sensor – online analysis

METROLOGY for HYDROGEN VEHICLES 2

 **Bundesamt
für Eich- und
Vermessungswesen**
Physikalisch-technischer Prüfdienst (PTP)

nel
flow measurement
services

 **Air Liquide**
creative oxygen

FROM RESEARCH TO INDUSTRY
cea

ENGIE

 **CEAME-**
exadébit sa

métrologie française
LNE-LADG
French Designated Institute
for high-pressure gas flow metering

EMCEL Engineering Company for Fuel Cell
Hydrogen Technology and Electric Mobility

 **Empa**
Materials Science and Technology

 **ITM POWER**
Energy Storage | Clean Fuel

Justervesenet 

 **METAS**




TOYOTA

NPL 
National Physical Laboratory

**RI
SE**

VTT

 **ZBT**

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EMPIR



EURAMET 

Thanks a lot,



any questions

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