CRÉER LA CONFIANCE LNE

ISO TC197 WG27/WG28

Metrology research for hydrogen standardisation: a cross-cutting approach

09 – 10th October 2018

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EMPIR : European programme for metrology research

EMPIR

EURAMET

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

EMPIR stands for European Metrology Programme for Innovation and Research

The programme arrange the cooperation between National Metrology Institutes in Europe and industries, academic laboratories and research centres in **Joint Research Projects (JRP)**

1st JRP granted on hydrogen topic of the Programme (2014-2020)

- In a new call in 2015: **Pre- and co-normative call** to bring forward the standardization needs in R&D related to metrology
- Standardization is recognized both as a great **recovery tool for research** and an **innovation dissemination vector**

→ Metrology for Sustainable Hydrogen Energy Applications

Hydrogen

Project data summary

- 2016- 2019
- Coordination: LNE
- All the partners involved in standardization work at national or international level

10 partners: 5 NMI + 5 industrial and research centres

Advisory board: 12 stakeholders

Project outputs towards…

Hydrogen

… Standardisation

- Input to **ISO/TC 197** "Hydrogen Technologies", **CEN/TC 268/WG 5** "Specific hydrogen technologies applications". Liaison with **CEN/CLC/JTC 6** "Hydrogen in Energy Systems"
- In-progress work presentations at national mirror committees
- Mandatory reporting documents to ISO/TC 197

… Metrology

- **Traceable impurity measurements** of hydrogen samples from SMR, electrolysis and chlor-alkali plants
- **Validated analytical methods** to comply with ISO 14687 in routine laboratory analyses
- **Validated method** to determine the hydrogen mass absorbed in metal hydrides

… Industries

- Production process for **hydrogen suppliers**
- Anticipation of the degradation risk for **fuel cell manufacturers**
- Improved analytical methods for **gas analyser manufacturers**
- High level of reliability of hydrogen mass stored in containers for **tank suppliers**

Metrology research studies for ISO standards input contribution

Hydrogen

Hydrogen purity measurements according to ISO 14687-2 and risk assessment for fuel cells

ISO 14687-2 (revision)

Hydrogen fuel - Product specification – Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles

ISO 19880-8 (new)

Gaseous hydrogen - Fuelling stations -- Part 8: Fuel quality control

Validated analytical methods to fulfill ISO 14687-2 impurity specifications

ISO 21087 (new)

Gas analysis -- Analytical methods for hydrogen fuel -- Proton exchange membrane (PEM) fuel cell applications for road vehicles

Traceable methods for mass measurements of hydrogen absorbed in metal hydrides

ISO 16111 (revision)

Developing transportable gas storage devices - Hydrogen absorbed in reversible metal hydride

Under the responsibility of ISO TC 197 "Hydrogen technologies"

Hydrogen purity measurements according to ISO 14687-2 and risk assessment for fuel cells

Probability of impurity presence from expert industrial knowledge

+

Sampling hydrogen on sites and analysis campaign at NMIs

+

Impact of trace concentration impurities on PEMFC performance

For hydrogen fuel quality and fuel quality control compliance ISO 14687-2 and ISO 19880-8

Hydrogen fuel quality and risk assessment for fuel cells

Hydrogen

Probability of impurity presence from expert industrial knowledge

Rationale of impurities presence based on production process and following an approach in ISO 19880.

Probability of impurity presence	Steam methane reforming with PSA	PEM water electrolysis process with TSA	Chlor-alkali process (membrane cell process)
Frequent	CO	None identified	O_2
Possible	N_2	None identified	None identified
Rare	Ar, CH_4	N_2, O_2, H_2O	H_2O, N_2
Very Rare	HCHO	CO_2	CO_2
Unlikely	H_2O, He, O_2, CO_2, HCOOH, NH_3, sulfur compounds, hydrocarbons (except CH_4), halogenated compounds	He, Ar, CO, CH_4, HCHO, HCOOH, NH_3, sulfur compounds, hydrocarbons (except CH_4), halogenated compounds	He, Ar, CO, CH_4, HCHO, HCOOH, NH_3, sulfur compounds, hydrocarbons (except CH_4), halogenated compounds

<u>Article published in peer reviewed article:</u>

Probability of occurrence of ISO 14687-2 contaminants in hydrogen: Principles and examples from steam methane reforming and electrolysis (water and chlor-alkali) production processes model

Thomas Bacquart, Arul Murugan, Martine Carré, Bruno Gozlan, Fabien Auprêtre, Frédérique Haloua, Thor A. Aarhaug

International Journal of Hydrogen Energy, 2018, 43 (11872-11883)

Air Liquide creative oxygen · NPL National Physical Laboratory · AREVA H2Gen

Hydrogen fuel quality and risk assessment for fuel cells

Hydrogen

Analytical campaign – Summary – Hydrogen production methods

Compounds	ISO 14687-2 threshold [µmol/mol]	SMR with PSA (6 samples) Results [µmol/mol]	PEM water electrolysis with TSA (7 samples) Results [µmol/mol]
Water H_2O	5	< 0.5 – 2.5	< 3
Methane CH_4	2	< 0.02 – 0.05	< 0.02
Non methane hydrocarbons	2	< 0.05	0.08 – 0.2
Oxygen O_2	5	< 0.5	< 0.5 - 2
Helium He	300	< 50	< 9 - 45
Nitrogen N_2	100	< 1.2 - 2	< 1.0 – 4.6
Argon Ar	100	< 0.5	< 0.5
Carbon dioxide CO_2	2	< 0.02 – 0.45	< 0.02 – 0.25
Carbon monoxide CO	0.2	< 0.02	< 0.02
Total sulphur compounds	0.004	< 0.0036	< 0.0036
Formaldehyde HCHO	0.01	< 0.005	< 0.005
Formic acid HCOOH	0.2	< 0.1	< 0.1
Ammonia NH_3	0.1	< 0.1	< 0.1
Total halogenated	0.05	< 0.005	< 0.005
C2 hydrocarbons	2	< 0.5	< 0.5
C3 hydrocarbons	2	<1	<1
C4 hydrocarbons	2	<1	<1
C5 hydrocarbons	2	<1	<1
C6 - C18 hydrocarbons	2	<0.05	<0.05

NPL National Physical Laboratory · RISE Research Institutes of Sweden · CEM Centro Español de Metrología · VSL Dutch Metrology Institute

Hydrogen fuel quality and risk assessment for fuel cells

Hydrogen

Analytical campaign – Summary – PEM water electrolysis

Compounds	ISO 14687-2 threshold [µmol/mol]	PEM water electrolysis with TSA (7 samples) Results [µmol/mol]	PEM water electrolysis (5 samples) Results [µmol/mol]
Water H_2O	5	< 3	> 100
Methane CH_4	2	< 0.02	< 0.02 – 0.1
Non CH_4 hydrocarbons	2	0.08 – 0.2	< 0.02 – 0 .09
Oxygen O_2	5	< 0.5 - 2	18- > 500
Helium He	300	< 9 - 45	< 9
Nitrogen N_2	100	< 1.0 – 4.6	1.2 – 4.5
Argon Ar	100	< 0.5	< 0.5
Carbon dioxide CO_2	2	< 0.02 – 0.25	0.2 – 5.4
Carbon monoxide CO	0.2	< 0.02	< 0.02
Total sulphur compounds	0.004	< 0.0036	< 0.0036
Formaldehyde HCHO	0.01	< 0.005	< 0.005
Formic acid HCOOH	0.2	< 0.1	< 0.1
Ammonia NH_3	0.1	< 0.1	< 0.1
Total halogenated	0.05	< 0.005	< 0.005
C2 hydrocarbons	2	< 0.5	< 0.5
C3 hydrocarbons	2	<1	<1
C4 hydrocarbons	2	<1	<1
C5 hydrocarbons	2	<1	<1
C6 - C18 hydrocarbons	2	<0.05	<0.05

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Hydrogen fuel quality and risk assessment for fuel cells

Sampling

Industrial experts

Analysis and uncertainty measurements of hydrogen from SMR, electrolysis and chlor-alkali plants by NMIs

1. Probability of impurity existence

2. Report of analysis campaign
   - 10 samples of SMR
   - 10 samples of electrolysis
   - 1 sample of chlor-alkali

Risk assessment of hydrogen impurities

3. Validation of the probability of impurity existence

Evidence for ISO 14687-2 revision
Supplementation for ISO 19880-8 elaboration

Hydrogen fuel quality and risk assessment for fuel cells

Hydrogen

Analytical campaign – Summary – PEM water electrolysis without purification

Probability of impurity presence	risk assessment by experts	Analytical campaign	Risk of occurrence confirmed
Water	2	all values above ISO 14687-2 threhold	purification needed
CH4	0	Confirmed, all samples below ISO 14687-2 threshold	0
Total hydrocarbon	0	Confirmed, all samples below ISO 14687-2 threshold	0
oxygen	2	all values above ISO 14687-2 threshold	purification needed
helium	0	Confirmed, all samples below ISO 14687-2 threshold	0
N2	2	Confirmed, all samples below ISO 14687-2 threshold	2
Ar	0	Confirmed, all samples below ISO 14687-2 threshold	0
CO	0	Confirmed, all samples below ISO 14687-2 threshold	0
CO2	1	some samples above ISO 14687-2 threshold	purification needed
Total S	0	*Confirmed, all samples below ISO 14687 threshold	0
Formaldehyde	0	*Confirmed, all samples below ISO 14687-2 threshold	0
Formic acid	0	*Confirmed, all samples below ISO 14687-2 threshold	0
Ammonia	0	*Confirmed, all samples below ISO 14687-2 threshold	0
HCl	0	Confirmed, all samples below ISO 14687-2 threshold	0

*: LOD is too high for perfect assessment (better analytical method required)

Hydrogen fuel quality and risk assessment for fuel cells

Analytical campaign – Summary – PEM water electrolysis + TSA

Probability of impurity presence	risk assessment by experts	Analytical campaign	Risk of occurrence confirmed
Water	2	Confirmed, all samples below ISO 14687-2 threshold	2
CH4	0	Confirmed, all samples below ISO 14687-2 threshold	0
Total hydrocarbon	0	Confirmed, all samples below ISO 14687-2 threshold	0
oxygen	2	Confirmed, all samples below ISO 14687-2 threshold	2
helium	0	Confirmed, all samples below ISO 14687-2 threshold	0
N2	2	Confirmed, all samples below ISO 14687-2 threshold	2
Ar	0	Confirmed, all samples below ISO 14687-2 threshold	0
CO	0	Confirmed, all samples below ISO 14687-2 threshold	0
CO2	1	Confirmed, all samples below ISO 14687-2 threshold	1
Total S	0	*Confirmed, all samples below ISO 14687 threshold	0
Formaldehyde	0	*Confirmed, all samples below ISO 14687-2 threshold	0
Formic acid	0	*Confirmed, all samples below ISO 14687-2 threshold	0
Ammonia	0	*Confirmed, all samples below ISO 14687-2 threshold	0
HCl	0	Confirmed, all samples below ISO 14687-2 threshold	0

*: LOD is too high for perfect assessment (better analytical method required)

Analytical campaign – Summary – Steam methane reforming with PSA

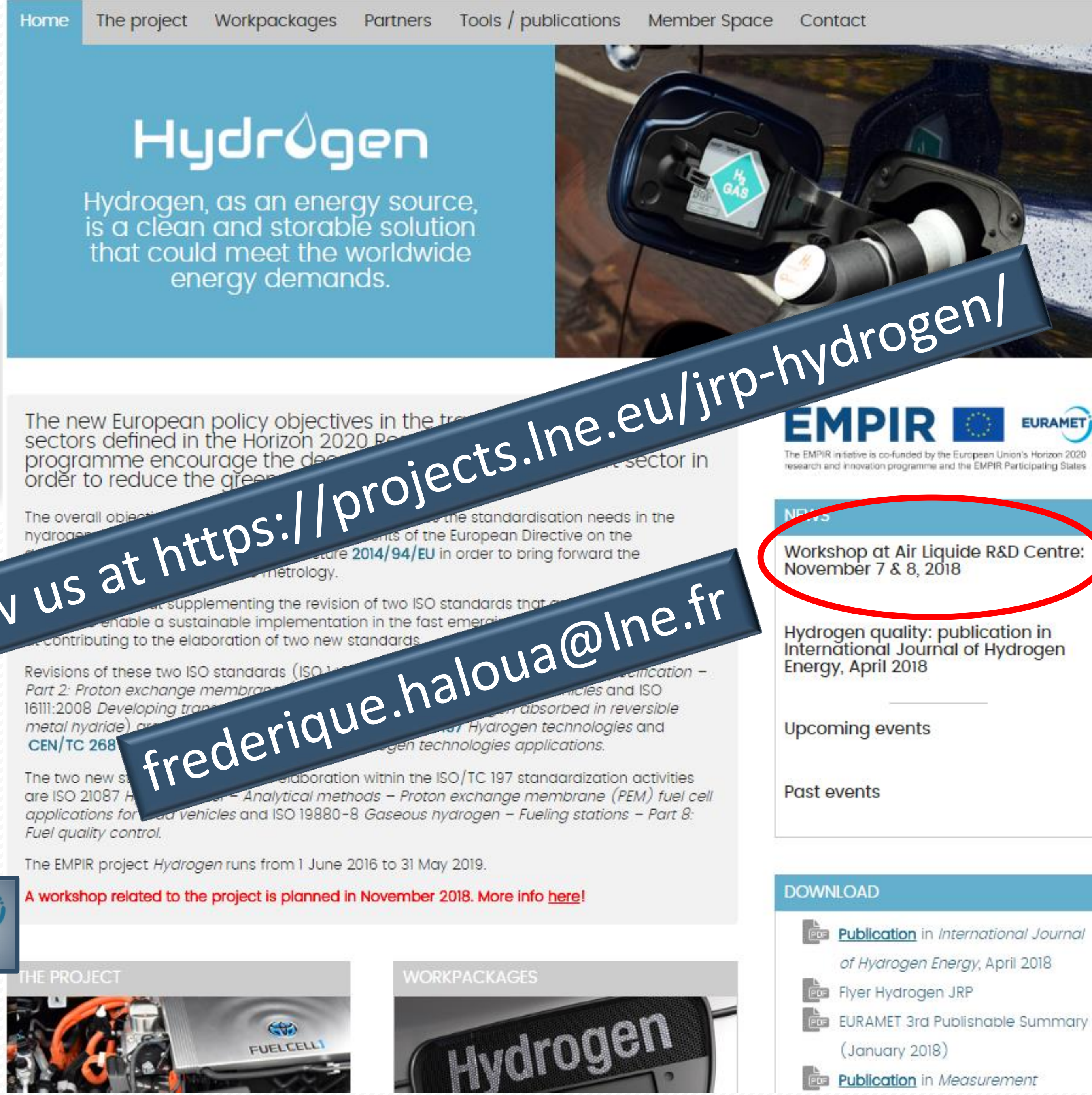
Probability of impurity presence	risk assessment by experts	Analytical campaign	Risk of occurrence confirmed
water	0	Confirmed, all samples below ISO 14687-2 threshold	0
CH4	2	Confirmed, all samples below ISO 14687-2 threshold	2
Total hydrocarbon	0	Confirmed, all samples below ISO 14687-2 threshold	0
oxygen	0	Confirmed, all samples below ISO 14687-2 threshold	0
helium	0	Confirmed, all samples below ISO 14687-2 threshold	0
N2	3	All samples below ISO 14687-2 threshold	3
Ar	2	All samples below ISO 14687-2 threshold	2
CO	4	All samples below ISO 14687-2 threshold	4
CO2	0	Confirmed, all samples below ISO 14687-2 threshold	0
Total S	0	*Confirmed, all samples below ISO 14687 threshold	0
Formaldehyde	1	*Confirmed, all samples below ISO 14687-2 threshold	1
Formic acid	0	*Confirmed, all samples below ISO 14687-2 threshold	0
Ammonia	0	*Confirmed, all samples below ISO 14687-2 threshold	0
HCl	0	Confirmed, all samples below ISO 14687-2 threshold	0

*: LOD is too high for perfect assessment (better analytical method required)

Traceable method for hydrogen mass measurements in metal hydride tanks

Results and future work

- Probability of impurity existence performed by industrial expert
  - Agreement with analytical campaign
  - Difficulty to observe discrete contamination (i.e. purging problem: nitrogen and Ar) during the analytical campaign
- Model and probability validated by sampling campaign
  - Reference for steam methane reforming with PSA and PEM Water electrolysis and TSA
  - Peer reviewed paper
- Report on risk assessment of impurities in hydrogen for fuel cells and recommendations on maximum concentration of individual compounds based on the new fuel cell degradation studies and on the probability of presence
- Future: Extension to the complete supply chain → future project?



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