NPL

INTERNATIONAL WORKSHOP

Metrology for sustainable hydrogen energy applications

Impurities found in real hydrogen production samples

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Probability of impurity presence from expert industrial knowledge

Hydrogen
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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	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 H_2Gen SINTEF

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

Probability of impurity presence from expert industrial knowledge

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Sampling hydrogen on sites and analysis campaign at NMIs

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Impact of trace concentration impurities on PEMFC performance

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

Analytical campaign for hydrogen production methods

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Analytical method used by National Metrology Institutes

Compounds	ISO 14687-2 threshold [µmol/mol]	NPL National Physical Laboratory	VSL Dutch Metrology Institute	RISE Research Institutes of Sweden	CEM Centro Español de Metrología
Water H_2O	5	Quartz crystal microbalance	-	-	-
Methane CH_4	2	GC-methaniser-FID	-	GC-FID	-
Non methane hydrocarbons	2	GC-methaniser-FID	-	GC-FID	-
Oxygen O_2	5	GC-PDHID	-	GC-TCD	GC-TCD
Helium He	300	-	-	-	GC-TCD
Nitrogen N_2	100	GC-PDHID	-	GC-TCD	GC-TCD
Argon Ar	100	GC-PDHID	-	GC-TCD	GC-TCD
Carbon dioxide CO_2	2	GC-methaniser-FID	-	OFCEAS	-
Carbon monoxide CO	0.2	GC-methaniser-FID	-	OFCEAS	-
Total sulphur compounds	0.004	GC-SCD	-	OFCEAS	-
Formaldehyde HCHO	0.01	-	CRDS	-	-
Formic acid HCOOH	0.2	-	CRDS	-	-
Ammonia NH_3	0.1	-	CRDS	-	-
Total halogenated (HCl)	0.05	-	CRDS	-	-
C2 hydrocarbons	2	-	-	TD-GC-FID/MS	-
C3 hydrocarbons	2	-	-	TD-GC-FID/MS	-
C4 hydrocarbons	2	-	-	TD-GC-FID/MS	-
C5 hydrocarbons	2	-	-	TD-GC-FID/MS	-
C6 - C18 hydrocarbons	2	-	-	TD-GC-FID/MS	-

GC: gas chromatography
PDHID: Pulse discharge helium ionisation detector
FID: Flame ionisation detector

CRDS: cavity ring down spectroscopy
TCD: Thermal Conductivity Detector
OFCEAS: Optical Feedback cavity enhanced adsorption spectroscopy

TD: Thermo-Desorption
MS: Mass spectrometry

Hydrogen fuel quality from production methods (1)

Analytical campaign – Summary – Hydrogen production methods

Compounds	ISO 14687-2 threshold [µmol/mol]	SMR with PSA (5 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

Hydrogen fuel quality from production methods (2)

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

Steam methane reforming with pressure swing adsorption - Analysis results

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		ISO 14687-2 threshold	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Contaminants	Unit		Results with expanded uncertainty (k=2)				
CO	µmol/mol	0.2	< 0.01	< 0.01	< 0.01	< 0.053	< 0.053
CO_2	µmol/mol	2	< 0.01	< 0.01	< 0.01	0.042 ± 0.016	< 0.02
CH_4	µmol/mol	2	< 0.01	< 0.01	< 0.01	0.044 ± 0.007	< 0.02
Non methane hydrocarbons	µmol/mol	2	< 0.01	< 0.01	< 0.01	< 0.05	< 0.05
H_2O	µmol/mol	5	< 0.5	< 0.5	< 0.5	< 0.6	< 0.6
Total sulphur compounds	µmol/mol	0.004	< 0.0036	< 0.0036	< 0.0036	< 0.002	< 0.002
O_2	µmol/mol	5	< 0.5	< 0.5	< 0.5	0.39 ± 0.13	0.39 ± 0.13
N_2	µmol/mol	100	< 1.2	< 1.2	< 1.2	1.5 ± 0.6	< 1.0
Ar	µmol/mol	100	< 0.5	< 0.5	< 0.5	2.8 ± 0.1	< 0.5
Total halogenated (HCl)	µmol/mol	0.05	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
CH_2O	µmol/mol	0.01	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
CH_2O_2	µmol/mol	0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
NH_3	µmol/mol	0.1	n.m.	< 0.1	< 0.1	< 0.1	< 0.1
He	µmol/mol	300	n.m.	n.m.	< 50	20 ± 4	12 ± 5
C2 hydrocarbons	µmol/mol	2	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
C3-hydrocarbons	µmol/mol	2	<1	<1	<1	<1	<1
C4-hydrocarbons	µmol/mol	2	<1	<1	<1	<1	<1
C5-hydrocarbons	µmol/mol	2	<1	<1	<1	<1	<1
C6 – C18 hydrocarbons	µmol/mol	2	<0.050	<0.050	<0.050	<0.050	<0.050

PEM water electrolyser with temperature swing adsorption - Analysis results

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		ISO 14687-2 threshold	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
	Unit		Results with expanded uncertainty (k=2)							
CO	µmol/mol	0.2	< 0.053	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
CO_2	µmol/mol	2	0.443 ± 0.010	0.245 ± 0.010	0.229 ±	< 0.02	< 0.02	< 0.01	< 0.01	< 0.01
CH_4	µmol/mol	2	0.031 ± 0.006	< 0.01	< 0.01	< 0.02	< 0.02	< 0.01	< 0.01	< 0.01
Non methane hydrocarbons	µmol/mol	2	< 0.05	< 0.02	< 0.02	< 0.02	< 0.02	0.156 ±	0.126 ±	0.111 ± 0.024
H_2O	µmol/mol	5	< 0.6	< 0.8	< 1.4	< 3	< 3	< 0.8	< 1.2	< 3
Total sulphur compounds	µmol/mol	0.004	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.0030	< 0.0030	< 0.0030
O_2		5	0.45 ± 0.13	< 0.5	< 0.5	< 0.6	< 0.6	1.39 ± 0.36	< 0.5	1.59 ± 0.45
N_2	µmol/mol	100	2.0 ± 0.5	4.6 ± 0.3	4.2 ± 0.4	< 1.5	< 1.5	1.51 ± 0.2	< 1.0	1.86 ± 0.2
Ar	µmol/mol	100	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Total halogenated (HCl)	µmol/mol	0.05	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	n.a.	< 0.005	< 0.005
CH_2O	µmol/mol	0.01	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
CH_2O_2	µmol/mol	0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
NH_3	µmol/mol	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	n.a.	n.a.	n.a.
He	µmol/mol	300	34 ± 5	< 5	< 5	15 - 45	< 5	< 9	< 9	< 9
C2 hydrocarbons	µmol/mol	2	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-	-	-
C3-hydrocarbons	µmol/mol	2	<1	<1	<1	<1	<1	-	-	-
C4-hydrocarbons	µmol/mol	2	<1	<1	<1	<1	<1	-	-	-
C5-hydrocarbons	µmol/mol	2	<1	<1	<1	<1	<1	-	-	-
C6 – C18 hydrocarbons	µmol/mol	2	<0.050	<0.05	<0.05	<0.05	<0.05	-	-	-

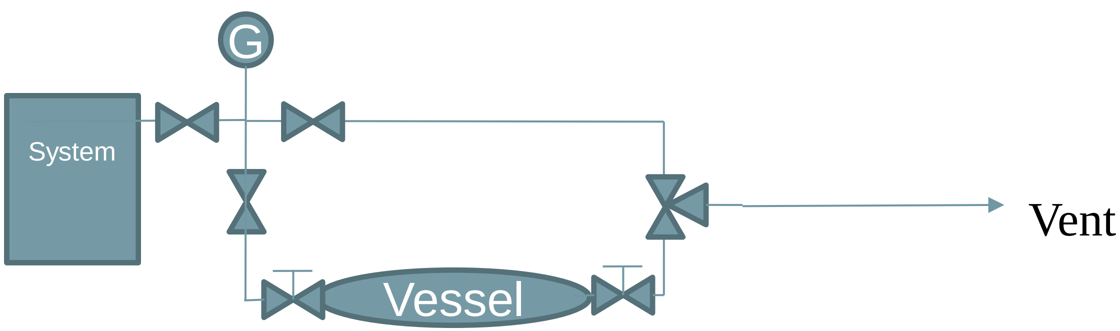
Hydrogen fuel quality from production methods - summary

- No contaminants observed above ISO 14687-2 threshold
  - 5 different sample from steam methane reformers with PSA
  - 8 different samples from PEM water electrolyser with TSA
- Challenges and additional contamination sources
  - Sampling
  - Hydrogen refuelling station infrastructure
  - Maintenance procedure

Sampling challenges

- Development of sampling strategy
  - Sampling
    - Pressure (14 – 100 bar)
    - Flow
    - Location (as close as production)
    - Sampling material
    - Sampling procedure

→ **EMPIR Hydrogen consortium**
Hydrogen producer procedure



- Cycling purge
- Purge through cylinder
- Cleanliness of cylinder
- Absence of leak

Example of contaminants observed in real samples

		Results with expanded uncertainty (k=2)	Results with expanded uncertainty (k=2)	Results with expanded uncertainty (k=2)	Results with expanded uncertainty (k=2)
CO	µmol/mol	< 0.02	< 0.02	< 0.053	< 0.02
CO_2	µmol/mol	4.2 ± 0.3	< 0.01	0.101 ± 0.004	0.316 ± 0.007
CH_4	µmol/mol	< 0.02	< 0.01	< 0.02	14.28 ± 0.07
Non methane hydrocarbons	µmol/mol	0.08 ± 0.01	0.111 ± 0.024	< 0.05	> 200
H_2O	µmol/mol	**> 500**	**> 250**	2.48 ± 0.25	13.2 ± 1.7
Total sulphur compounds	µmol/mol	< 0.002	< 0.0030	< 0.002	< 0.0036
O_2	µmol/mol	**> 520**	1.59 ± 0.45	**35 ± 2**	< 0.5
N_2	µmol/mol	3.7 ± 0.8	1.86 ± 0.2	**134 ± 2**	579 ± 23
Ar	µmol/mol	< 0.5	< 0.5	**1.43 ± 0.10**	< 1.0
Total halogenated (HCl)	µmol/mol	< 0.005	< 0.005	< 0.005	< 0.0036
CH2O	µmol/mol	< 0.005	< 0.005	< 0.005	< 0.005
CH2O2	µmol/mol	< 0.1	< 0.1	< 0.1	< 0.1
NH3	µmol/mol	< 0.1	n.a.	< 0.1	< 0.1
He	µmol/mol	< 5	< 9	< 5	< 20

Electrolyser without purification

Sampling contamination (air, humidity)

HRS maintenance contamination suspected

Summary and futures perspectives

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- No contaminants observed above ISO 14687-2 threshold from current production methods
  - SMR with PSA samples
  - PEM water electrolyser with TSA samples

- Challenges on contamination sources
  - Sampling
  - Hydrogen refuelling station infrastructure
  - Maintenance procedure

  → Analytical evidences needed

- 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

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EMPIR EURAMET

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