



Metrology research for hydrogen standardisation: a cross-cutting approach

Training course

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

Training course - 07 November 2018

Air Liquide R&D – Versailles - France



- Overview of hydrogen quality requirements
- Quality control plan
- Monitoring / Sampling



Overview of hydrogen quality requirements – 5 min

Quality control plan

Presentation

Exercise

Restitution

- 15 min

- 20 min

- 10 min

Monitoring / Sampling

Presentation

- 10 min

Exercise

- 10 min

Summary / Discussion / Questions

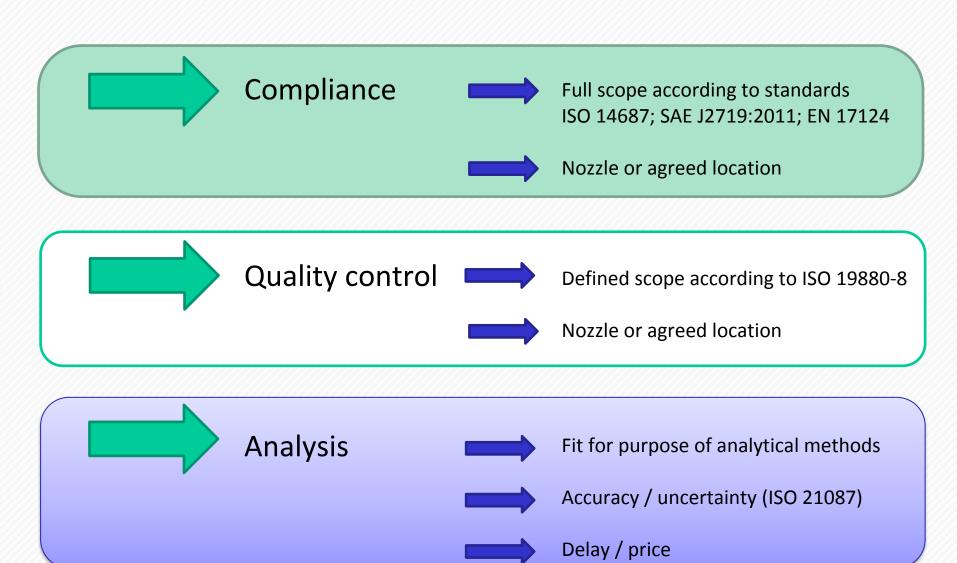
5 min



- Overview of hydrogen quality requirements
- Quality control plan
- Monitoring / Sampling

Hydrogen quality for fuel cell electrical vehicles



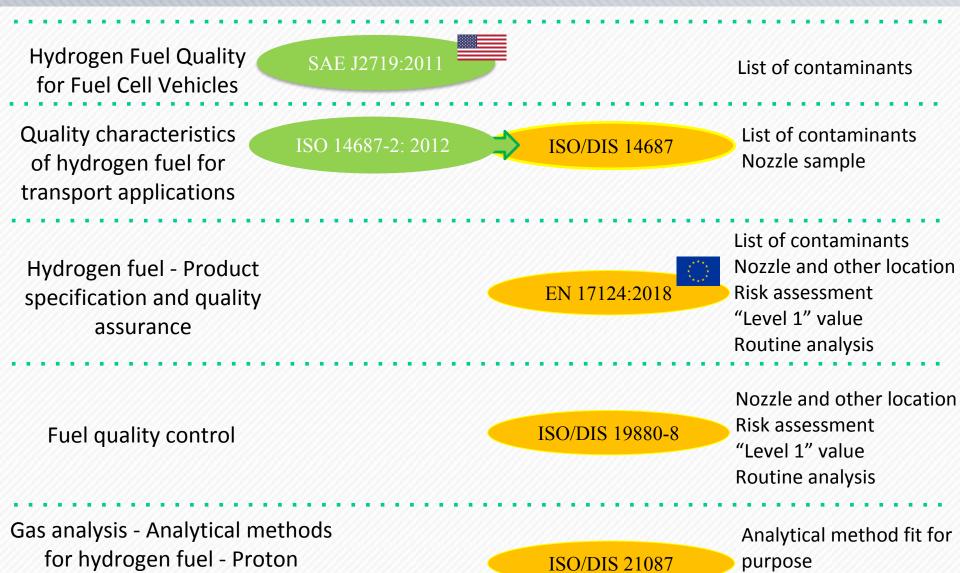


Existing normative documents for fuel cell vehicles

exchange membrane (PEM) fuel

cell applications for road vehicles





6

Method validation

Reporting

Technical challenges linked to ISO 14687



	ISO 14687: 2012	/ SAE J2719:2011	ISO/C	D 14687 / EN 17124
	Max. admissible value [μmol/mol]	notes	Max. admissible value [μmol/mol]	notes
Water	5		5	
Total hydrocarbons (TC)	2	Due to CH ₄ , TC > 2 μmol/mol	2 except CH ₄	including oxygenated organic species
Methane	-		100	
Oxygen	5		5	
Helium	300		300	
Nitrogen	100	N ₂ +Ar<100	300	
Argon	100	N ₂ +Ar<100	300	
carbon dioxide	2		2	
Carbon monoxide	0.2		0.2	CO+HCHO+HCOOH < 0.2μmol/mol
Total sulphur compounds	0.004	H ₂ S, COS, CS ₂ , mercaptans (NG)	0.004	H ₂ S, COS, CS ₂ , mercaptans (NG)
Formaldehyde	0.01		0.2	CO+HCHO+HCOOH < 0.2μmol/mol
Formic acid	0.2		0.2	CO+HCHO+HCOOH < 0.2μmol/mol
Ammonia	0.1		0.1	
Halogenated compounds	0.05 (total)	i.e. HBr, HCl Cl ₂ , organic R-X	0.05	HCl, organic R-Cl
Max. particulate conc.	1 mg/kg		1 mg/kg	

Technical challenges linked to ISO 14687



	ISO 14687: 2012	/ SAE J2719:2011	ISO/C	D 14687 / EN 17124
	Max. admissible value [μmol/mol]	notes	Max. admissible value [μmol/mol]	notes
Water	5		5	
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Methane	-		100	
Oxygen	5		5	
Helium	300		300	
Nitrogen	100	N ₂ +Ar<100	300	
Argon	100	N ₂ +Ar<100	300	
carbon dioxide	2		2	
Carbon monoxide	0.2		0.2	CO+HCHO+HCOOH < 0.2μmol/mol
Total sulphur compounds	0.004	H ₂ S, COS, CS ₂ , mercaptans (NG)	0.004	H ₂ S, COS, CS ₂ , mercaptans (NG)
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Ammonia	0.1		0.1	
Halogenated compounds	0.05 (total)	i.e. HBr, HCl Cl ₂ , organic R-X	0.05	HCI, organic R-CI
Max. particulate conc.	1 mg/kg		1 mg/kg	

Technical challenges linked to ISO 14687



	ISO 14687: 2012	/ SAE J2719:2011	ISO/C	D 14687 / EN 17124
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Water	5		5	
Total hydrocarbons (TC)	2	Due to CH ₄ , TC > 2 μmol/mol	2 except CH₄	including oxygenated organic species
Methane	-		100	
Oxygen	5		5	
Helium	300		300	
Nitrogen	100	N ₂ +Ar<100	300	
Argon	100	N ₂ +Ar<100	300	
carbon dioxide	2		2	
Carbon monoxide	0.2		0.2	CO+HCHO+HCOOH < 0.2µmol/mol
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Ammonia	0.1		0.1	
Halogenated compounds	0.05 (total)	i.e. HBr, HCl Cl ₂ , organic R-X	0.05	HCl, organic R-Cl
Max. particulate conc.	1 mg/kg		1 mg/kg	



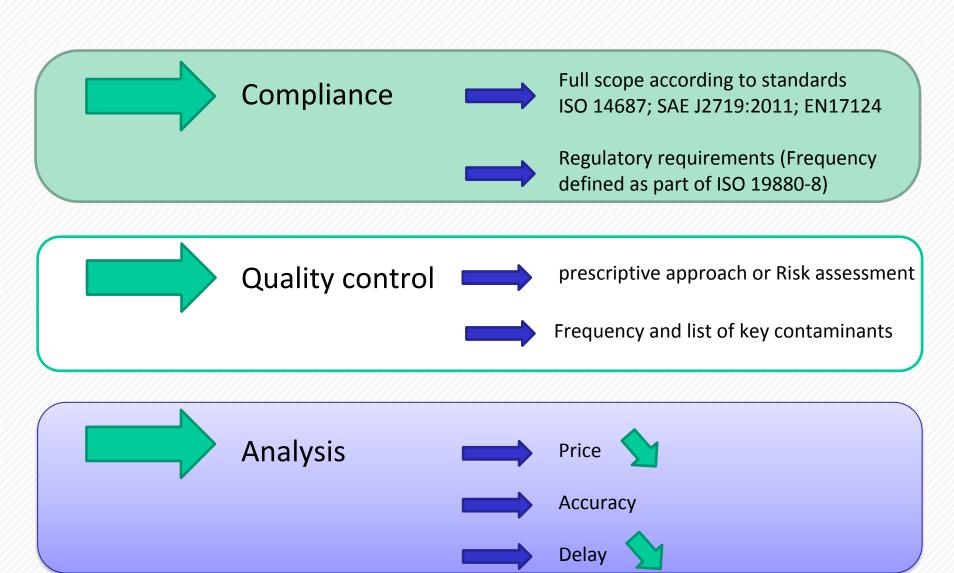
Price: 2000 – 6000 € / sample

Delay: 2 – 8 weeks



- Overview of hydrogen quality requirements
- Quality control plan
- Monitoring / Sampling





Quality control - Prescriptive approach



Prescriptive approach methodology

Quality analysis of the contaminants listed in ISO 14687:

- 1 Potential sources of contaminants
 - o Sampling procedures
 - o Characteristics of hydrogen production method(s)
 - o Characteristics of hydrogen transport method(s)
 - o Non-routine procedure (for example maintenance, major production system change)
- 2 Analysis of possible contaminants
 - o Possible quantification



Quality control - Prescriptive approach



Prescriptive approach methodology

- Production type
- Sampling point
- Frequency
 - Reduced frequency
 - Online monitoring / operation control
 - Not satisfied → analysis once a day

	Category: Distril	ution		
Facility type	Sampling/ Monitoring point	Contaminant	Threshold (µmol/mol)	Reduced frequency
		TSa	0,004	Annual
Production of hydrogen from		THC as C1	2	Annual
nydrocarbons utilizing steam reforming, catalytic reforming, partial oxidation, or	Downstream of the	СО	0,2	Annual
ATR, purification using refining	purifier	N2+Ar	100	Annual ^{b,c}
equipment, and distribution		H ₂ O	5	Annual
- 0.00		O ₂	5	Annual ^{b,c}
		Halogens	0,05	Annual
Electrolysis of Na Cl for hydrogen,	Downstream of the	N2+Ar	100	Annual
purification, and distribution	purifier	H ₂ O	5	Annual ^b
		O ₂	5	Annual
	Downstream of the	TS	0,004	Annual
		THC as C1	2	Annual
		CO	0,2	Annual
		Halogens	0,05	Annual
Purification of coke-oven gas, and		N ₂ +Ar	100	Annual
distribution	purifier	H ₂ O	5	Annual
		O ₂	5	Annual ^b
		NH ₃	0,1	Annual
		нсно	0,01	Annual
		HCOOH	0,2	Annual
		TS	0,004	Annual
		THC as C1	2	Annual
Purification of byproduct hydrogen	Downstream of the	CO	0,2	Annual
from ethylene plants, and distribution	purifier	N2+Ar	100	Annual ^b
		H ₂ O	5	Annual
		02	5	Annual

Quality control - Prescriptive approach



Prescriptive approach methodology

- Supply type
- Sampling point
- Frequency
 - Reduced frequency
 - Online monitoring / operation control
 - Not satisfied → analysis once a day

	Category: Fueling	station		
Facility type	Sampling/Monitoring point	Contaminant	Threshold (µmol/mol)	Reduced frequency
		Those not analysed by the distributor		Annual
With off-site supply of transported	End of nozzle	N2+Ar	100	Annual ^{b, c}
compressed or liquid hydrogen		H ₂ O	5	Annual ^{b,d}
		O ₂	5	Annual ^{b,c}
	Downstream of the deodorant equipment	(Those listed for the odorant)		Annual be
		Those not analysed by the distributor		Annual
With off-site supply from hydrogen		N2+Ar	100	Annual b.c
pipelines	End of nozzle	H ₂ O	5	Annual ^{b,d}
		O ₂	5	Annual ^{b,c}
	Downstream of the purifier	со	0,2	Continuous and Annual ^b
	End of nozzle	TS a	0,004	Annual
With on-site supply of hydrogen produced from hydrocarbons utilizing		THC as C1	2	Annual
steam reforming, catalytic reforming, partial oxidation, or ATR and purification using refining equipment		co	0,2	Annual
		N ₂ +Ar	100	Annual be
		H ₂ O	5	Annual ^{b,d}
		02	5	Annual be
		N ₂ +Ar	100	Annual
	Downstream of the	H ₂ O	5	Continuous and Annual ^b
	purnier	Oz	5	Continuous and Annual ^b
With on-site supply from hydroelectrolysis and purification using		Halogens	0,05	Annual
refining equipment	621770 DSS	N ₂ +Ar	100	Annual ^b
	End of nozzle	H2O	5	Annual
		O ₂	5	Annual



Risk assessment methodology





Severity class: impact on fuel cell electrical vehicles

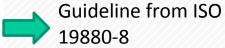
Table 2: Definition of severity classes

SEVERITY	FCEV Performance		Impact categories	
CLASS	impact or damage	Performance impact	hardware impact temporary	Hardware impact permanent
0	No impact	No	No	No
1	Minor impact temporary loss of power No impact on hardware Car still operates	Yes	No	No
2	Reversible damage Requires specific procedure, light maintenance. Car still operates.	Yes or No	Yes	No
3	Reversible damage Requires specific procedure and immediate maintenance. Gradual power loss that does not compromises	Yes	Yes	No
4	Irreversible damage Requires major repair (e.g. stack change). Power loss or Car Stop that compromises safety	Yes	Yes	Yes



Severity class: impact on fuel cell electrical vehicles

Impurity		Severity Class for 0 ppm ≤ Concentration < ISO Value	ISO 14687-2 Threshold Value ² [ppm]	Severity Class for ISO Value ≤ Concentration « Level 1 Value	Level 1 Value [ppm]	Severity Class for Level 1 Value ≤ Concentration ≤ 100%
Total non-H ₂ gases		0	300	1	300	4
Total Nitrogen and Argon	N ₂ , Ar	0	100	13	3003	4
Oxygen	02	0	5	No test data available		Without test data for proposed level 1 value validation already SC4 if ISO Spec exceeded
Carbon dioxide	CO2	0	2	1	3	4
Carbon monoxide	CO	0-2	0,2	2.34	1	4
Methane	CH ₄	0	100	1	300	4
Water	H ₂ 0	0	5	4) NA	Already SC4 if ISO Spec exceeded
Total sulfur compounds	H ₂ S basis	0-4	0.004	4	NA NA	Already SC4 if ISO Spec exceeded
Ammonia	NH ₃	0	0.1	4) NA	Already SC4 if ISO Spec exceeded
Total hydrocarbons	CH ₄ basis	0-4	2	1-4) NA	Already SC4 if ISO Spec exceeded
Formaldehyde	CH ₂ O	0	0.01	2-34	1	4
Formic Acid	CH ₂ O ₂	0-2	0.2	2-34) 1	4
Total halogenated compounds		0-4	0.05	4	NA NA	Already SC4 if ISO Spec exceeded
Helium	He	0	300	1	300	4
Maximum particulates concentration (liquid and solid)		0-4	1 mg/kg	4) NA	Already SC4 if ISO Spec exceeded



Influence on the severity class is complex and long term



Probability of occurrence of contaminants

Occurrence class	Class name	Occurrence or frequency	Occurrence or frequency
0	Very unlikely (practically impossible)	Contaminant above threshold never been observed for this type of source in the industry	Never
1	Very rare	Heard in the industry for the type of source / supply chain considered	1 per 1000000 refueling
2	Rare	Has happened more than once per year in the industry	1 per 100000 refueling
3	Possible	Has happened repeatedly for this type of source at a specific location	1 per 10000 refueling
4	Frequent	Happens on a regular basis	Often

Risk acceptability matrix



			Severity				
		0	1	2	3	4	
Occurrence as the	4						
combined	3						
probabilities of the occurrence	2						
along the whole	1						
supply chain	0						
Key	risk: ba	acceptable : additional irriers are equired	needed: barriers or	vestigation existing control may enough	Existing	e risk area: control otable	



Guideline from ISO 19880-8

System defined

Risk acceptability matrix



			Severity			
		0	1	2	3	4
Occurrence as the combined probabilities of the occurrence	4					
	3					
	2					
along the whole	1			7		
supply chain	0		A	dd barrier /	Control	
Key	risk ba	acceptable : additional irriers are equired	needed: barriers or o	vestigation existing control may enough	Existing	e risk area: control otable



Each HRS will have different controls or barriers:

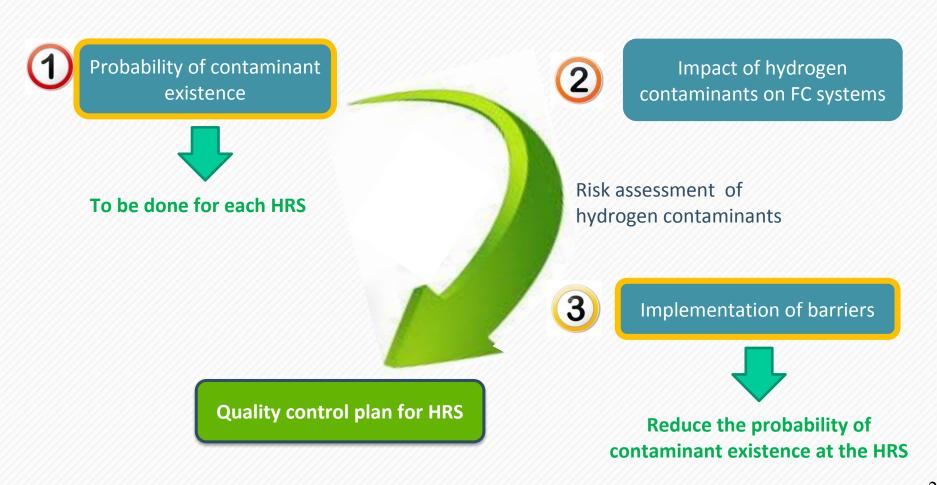
- Online sensors (i.e. hygrometers, CO sensor)
- Purification system
- Procedure (i.e. purging procedure after maintenance)
- Trained staff
- -



Each HRS will have a different risk assessment

Hydrogen fuel quality and risk assessment





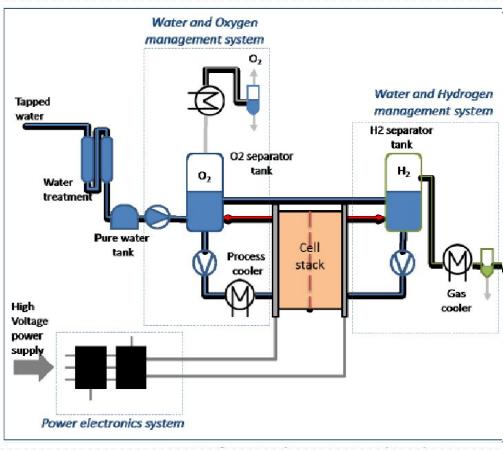


Probability of contaminants presence on PEM water electrolyser

- Implementation of barriers
- Monitoring



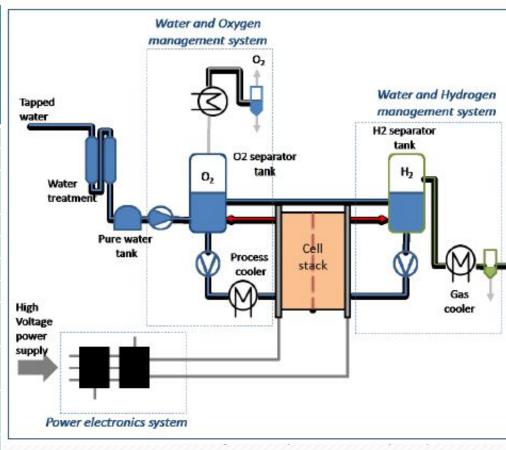
Compounds	ISO 14687-2 threshold [µmol/mol]	PEM water electrolysis (analysis) Results [µmol/mol]	Probability of occurrence [0-4]
Water H₂O	5	> 100	
Methane CH ₄	2	< 0.02 - 0.1	
Non CH ₄ hydrocarbons	2	< 0.02 - 0.09	
Oxygen O ₂	5	18- > 500	
Helium He	300	< 9	
Nitrogen N ₂	100	1.2 - 4.5	
Argon Ar	100	< 0.5	
Carbon dioxide CO ₂	2	0.2 – 5.4	
Carbon É monoxide CO	0.2	< 0.02	
Total sulphur compounds	0.004	< 0.0036	
Formaldehyde HCHO	0.01	< 0.005	
Formic acid HCOOH	0.2	< 0.1	
Ammonia NH ₃	0.1	< 0.1	
Total halogenated	0.05	< 0.005	



Question 1: What is the probability of contaminants presence on PEM water electrolyser (reply directly in the table)?



Compounds	ISO 14687-2 threshold [µmol/mol]	PEM water electrolysis (analysis) Results [µmol/mol]	Probability of occurrence [0-4]
Water H₂O	5	> 100	
Methane CH _₄	2	< 0.02 - 0.1	
Non CH ₄ hydrocarbons	2	< 0.02 - 0.09	
Oxygen O ₂	5	18- > 500	
Helium He	300	< 9	
Nitrogen N ₂	100	1.2 - 4.5	
Argon Ar [*]	100	< 0.5	
Carbon dioxide CO ₂	2	0.2 – 5.4	
Carbon monoxide CO	0.2	< 0.02	
Total sulphur compounds	0.004	< 0.0036	
Formaldehyde HCHO	0.01	< 0.005	
Formic acid HCOOH	0.2	< 0.1	
Ammonia NH ₂	0.1	< 0.1	
Total halogenated	0.05	< 0.005	



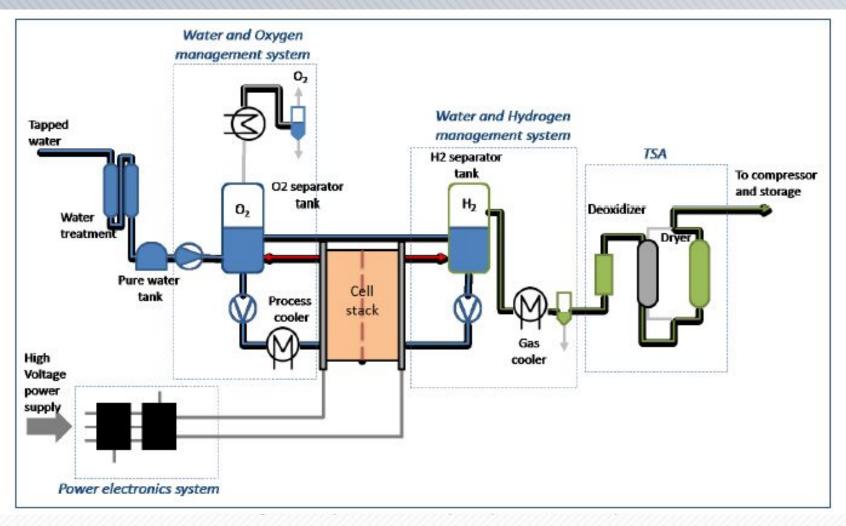
Question 2: What controls and barriers can be implemented based on your probability of occurrence?



Compounds	ISO 14687-2 threshold [µmol/mol]	PEM water electrolysis (analysis) Results [µmol/mol]	Probability of occurrence [0-4]	Controls and barriers	Probability of occurrence after control and barrier [0-4]
Water H ₂ O	5	> 100			
Methane CH ₄	2	< 0.02 - 0.1			
Non CH ₄ hydrocarbons	2	< 0.02 - 0 .09			
Oxygen O ₂	5	18- > 500			
Helium He	300	< 9			
Nitrogen N ₂	100	1.2 - 4.5			
Argon Ar -	100	< 0.5			
Carbon dioxide CO ₂	2	0.2 - 5.4			
Carbon monoxide CO	0.2	< 0.02			
Total sulphur compounds	0.004	< 0.0036			
Formaldehyde HCHO	0.01	< 0.005			
Formic acid HCOOH	0.2	< 0.1			
Ammonia NH ₂	0.1	< 0.1			
Total halogenated	0.05	< 0.005			

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Question 3: What controls and barriers would you add on this system?

Reply directly on the schematic



Question 4: What differences do you observe between your probability of occurrence and this results?

Probability of impurity presence	PEM water electrolysis process with TSA		
Frequent	None identified		
Possible	None identified		
Rare	N ₂ , O ₂ , H ₂ O		
Very Rare	CO ₂		
Unlikely	He, Ar, CO, CH ₄ , HCHO, HCOOH, NH ₃ , sulfur compounds, hydrocarbons (except CH ₄), halogenated compounds		

Differences:

Explanations:



Discussion / Feedback from groups



- Overview of hydrogen quality requirements
- Quality control plan
- Monitoring / Sampling



Hydrogen quality monitoring

- Online analysers / Sensors
 - Pressure
 - Flow
 - Location
 - Maintenance
 - Calibration



Sampling

- Pressure
- Flow
- Location
- Sampling material
- Sampling procedure



Monitoring / Sampling



Hydrogen quality monitoring

- Online analysers / Sensors
 - Pressure
 - Flow
 - Location
 - Maintenance
 - Calibration

- Humidity
 - O₂ CO
 - CH₄ CO₂

- Sampling
 - Pressure
 - Flow
 - Location
 - Sampling material
 - Sampling procedure



Hydrogen quality monitoring

- Online analysers / Sensors
 - Pressure
 - Flow
 - Location
 - Maintenance
 - Calibration

- Humidity
 - O₂ CO
 - CH₄ CO₂

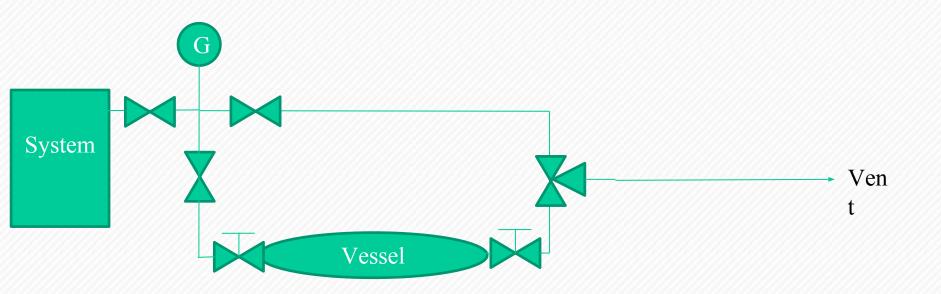
- Sampling
 - Pressure
 - Flow
 - Location
 - Sampling material
 - Sampling procedure



Eliminating contamination

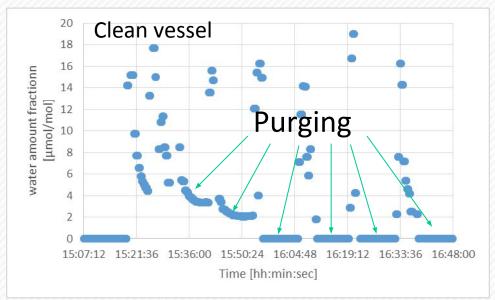
Monitoring / Sampling



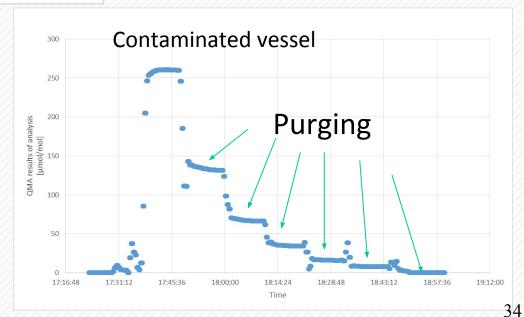


Monitoring / Sampling Humidity – water vapour





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



Monitoring / Sampling



Hydrogen quality monitoring

Online analysers / Sensors

- Pressure
- Flow
- Location
- Maintenance
- Calibration

Humidity

- 02
- CŌ
- CH₄
- CO_2

Sampling

- Pressure
- Flow
- Location
- Sampling material
- Sampling procedure

- Material of sampling system (passivated)
- Leak check
- Purge
- Procedure
- Trained staff
- Cylinder (transportable, passivated)



Example of issues with analytical results



		Results with expanded	Results with expanded	Results with expanded	Results with expanded
		uncertainty (k=2)	uncertainty (k=2)	uncertainty (k=2)	uncertainty (k=2)
СО	μmol/mol	< 0.02	< 0.02	< 0.053	< 0.053
CO ₂	μmol/mol	4.2 ± 0.3	< 0.01	0.101 ± 0.004	0.443 ± 0.010
CH₄	μmol/mol	< 0.02	< 0.01	< 0.02	0.031 ± 0.006
Non methane hydrocarbons	μmol/mol	0.08 ± 0.01	0.111 ± 0.024	< 0.05	< 0.05
H ₂ O	μmol/mol	> 500	> 250	2.48 ± 0.25	< 0.6
Total sulphur compounds	μmol/mol	< 0.002	< 0.0030	< 0.002	< 0.002
02	μmol/mol	> 520	1.59 ± 0.45	35 ± 2	0.45 ± 0.13
N ₂	μmol/mol	3.7 ± 0.8	1.86 ± 0.2	134 ± 2	2.0 ± 0.5
Ar	μmol/mol	< 0.5	< 0.5	1.43 ± 0.10	< 0.5
Total halogenated (HCI)	μmol/mol	< 0.005	< 0.005	< 0.005	< 0.005
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	<5

Question 1: What potential issues do you find in these analysis? Highlight the results of analysis that are suspicious

Question 2: Is there results of analysis that were contaminated by the sampling process?

Example of issues with analytical results



		ISO 14687-2 threshold	Results with expanded uncertainty (k=2)			
СО	μmol/mol	0.2	< 0.02	< 0.02	< 0.053	< 0.053
CO ₂	μmol/mol	2	4.2 ± 0.3	< 0.01	0.101 ± 0.004	0.443 ± 0.010
CH ₄	μmol/mol	2	< 0.02	< 0.01	< 0.02	0.031 ± 0.006
Non methane hydrocarbons	μmol/mol	2	0.08 ± 0.01	0.111 ± 0.024	< 0.05	< 0.05
H ₂ O	μmol/mol	5	> 500	> 250	2.48 ± 0.25	< 0.6
Total sulphur compounds	μmol/mol	0.004	< 0.002	< 0.0030	< 0.002	< 0.002
02	μmol/mol	5	> 520	1.59 ± 0.45	35 ± 2	0.45 ± 0.13
N ₂	μmol/mol	100	3.7 ± 0.8	1.86 ± 0.2	134 ± 2	2.0 ± 0.5
Ar	μmol/mol	100	< 0.5	< 0.5	1.43 ± 0.10	< 0.5
Total halogenated (HCI)	μmol/mol	0.05	< 0.005	< 0.005	< 0.005	< 0.005
CH2O	μmol/mol	0.01	< 0.005	< 0.005	< 0.005	< 0.005
CH2O2	μmol/mol	0.2	< 0.1	< 0.1	< 0.1	< 0.1
NH3	μmol/mol	0.1	< 0.1	n.a.	< 0.1	< 0.1
He	μmol/mol	300	< 5	< 9	< 5	<5
Reply question 2			Normal results or contaminated during sampling			
Reasons						

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Summary Sampling



Hydrogen monitoring

- Sampling
 - Pressure
 - Flow
 - Location
 - Sampling material
 - Sampling procedure

- Material of sampling system (passivated)
- Leak check
- Purge
- Procedure
- Trained staff
- Cylinder (transportable, passivated)



Typical issues:

- Air (ratio N₂ / O₂ / Ar)
- Humidity (high content)



- Leak check
- Purge
- Procedure
- Trained staff

Summary / Questions / Discussions



- Overview of hydrogen quality requirements
 - ISO 14687 Hydrogen quality
 - ISO 19880-8 Hydrogen quality control
- Quality control plan
 - Prescriptive
 - Risk assessment → for each HRS
 - Severity (fixed)
 - Probability of contaminant presence
 - Depend on system and barriers
- Monitoring / Sampling
 - Online
 - Sampling
 - Sampling system (passivated); cylinder (transportable, passivated)
 - Leak check
 - Purge
 - Procedure and trained staff

Contact

Hydr\0gen



Hydr@gen

Hydrogen, as an energy source, is a clean and storable solution that could meet the worldwide



frederique.haloua@lne.fr Part 2: Proton exchange membran 16111:2008 Developing trap metal hydride) a **CEN/TC 268**

The two new st are ISO 21087 A ad vehicles and ISO 19880-8 Gaseous hydrogen – Fueling stations – Part 8: applications for Fuel quality control.

The EMPIR project Hydrogen runs from 1 June 2016 to 31 May 2019.

A workshop related to the project is planned in November 2018. More info here!





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

FUELCELL



Workshop at Air Liquide R&D Centre:

research and innovation programme and the EMPIR Participating States.

Hydrogen quality: publication in International Journal of Hydrogen

Upcoming events

Past events

DOWNLOAD



Publication in International Journal of Hydrogen Energy, April 2018



Flyer Hydrogen JRP



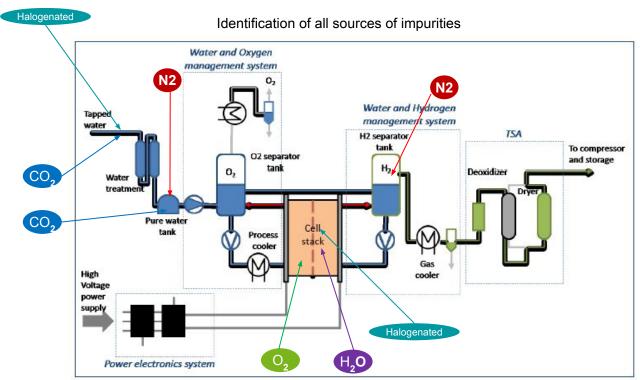
EURAMET 3rd Publishable Summary (January 2018)



Publication in Measurement



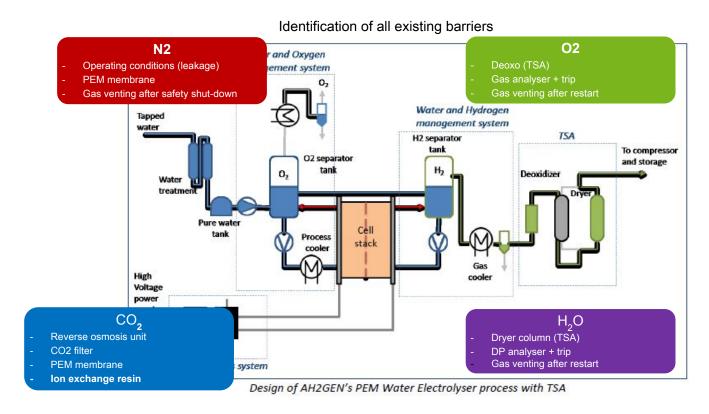
2 – PEM Electrolysis + TSA



Design of AH2GEN's PEM Water Electrolyser process with TSA



2 – PEM Electrolysis + TSA



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