METROLOGY for HYDROGEN VEHICLES

HYDRAITE

Hydrogen purity introduction

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EMPIR EURAMET FCH

Overview

- Applications of hydrogen
- Classification of hydrogen grades
- Fuel quality specifications
- Impact of impurities
- Hydrogen production
- Hydrogen purification

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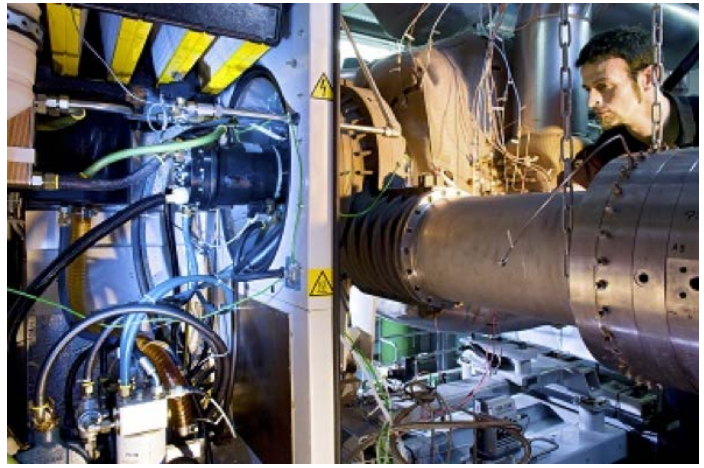
Applications of hydrogen fuel

- ICE
- Hydrogen turbine
- PEM technology



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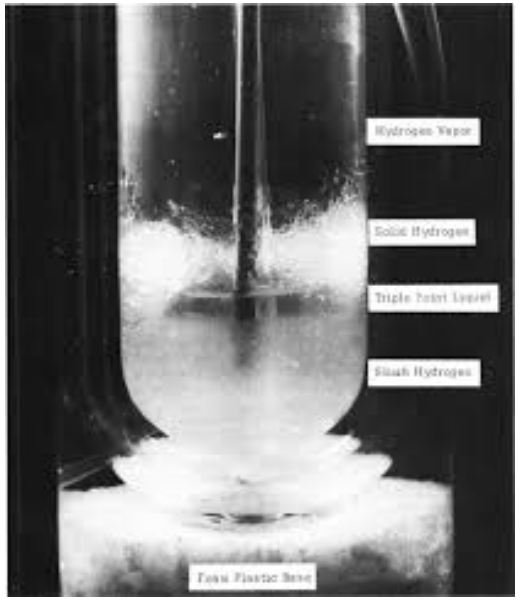
Classification of hydrogen

Type	Grade	Category	Applications
I Gas	A	—	Internal combustion engines for transportation; Residential/commercial combustion appliances (e.g. boilers, cookers and similar applications)
	B	—	Industrial fuel for power generation and heat generation except PEM fuel cell applications
	C	—	Aircraft and space-vehicle ground support systems except PEM fuel cell applications
	D	—	PEM fuel cells for road vehicles
	E	PEM fuel cells for stationary appliances	
		1	High efficiency/low power; minimum hydrogen fuel index of 50%
		2	High power; minimum hydrogen fuel index of 50%
		3	Hydrogen applications; minimum hydrogen fuel index of 99.9%
II Liquid	C	—	Aircraft and space-vehicle on-board propulsion and electrical energy requirements; Off-road vehicles.
	D	—	PEM fuel cells for road vehicles
III Slush	—	—	Aircraft and space-vehicle on-board propulsion

ISO 14687-2:2019



Slush hydrogen

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Fuel quality specification: non-PEM

Constituents (assay)	Type I			Type II	Type III
	Grade A	Grade B	Grade C	Grade C	
Hydrogen fuel index [a] (minimum mole fraction, %)	98,0 %	99,90 %	99,995 %	99,995 %	99,995 %
Para-hydrogen (minimum mole fraction, %)	NS	NS	NS	95,0 %	95,0 %
Impurities (maximum content)					
Total gases			50 µmol/mol	50 µmol/mol	
Water (mole fraction, %)	NC [b]	NC	c	c	
Total hydrocarbon	100 µmol/mol	NC	c	c	
Oxygen	b	100 µmol/mol	d	d	
Argon	b		d	d	
Nitrogen	b	400 µmol/mol	c	c	
Helium			39 µmol/mol	39 µmol/mol	
CO_2			e	e	
CO	1 µmol/mol		e	e	
Mercury		0,004 µmol/mol			
Sulfur	2,0 µmol/mol	10 µmol/mol			
Permanent particulates	g	f	f	f	
Density					f

NOTE 1 NS: Not specified

NOTE 2 NC: Not to be condensed

a The hydrogen fuel index is determined by subtracting the "total non-hydrogen gases" expressed in mole percent, from 100 mole percent.

b Combined water, oxygen, nitrogen and argon: maximum mole fraction of 1,9 %.

c Combined nitrogen, water and hydrocarbon: max. 9 µmol/mol.

d Combined oxygen and argon: max. 1 µmol/mol.

e Total CO_2 and CO: max. 1 µmol/mol.

f To be agreed between supplier and customer.

g The hydrogen shall not contain dust, sand, dirt, gums, oils, or other substances in an amount sufficient to damage the fuelling station equipment or the vehicle (engine) being fuelled.

ISO 14687-2:2019

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Fuel quality specification: PEM automotive

Constituents (assay)	Type I, Type II Grade D
Hydrogen fuel index (minimum mole fraction)[a]	99,97 %
Total non-hydrogen gases	300 µmol/mol
Maximum concentration of individual contaminants	
Water (H_2O)	5 µmol/mol
Total hydrocarbons except methane [b] (C1 equivalent)	2 µmol/mol
Methane (CH_4)	100 µmol/mol
Oxygen (O_2)	5 µmol/mol
Helium (He)	300 µmol/mol
Nitrogen (N_2)	300 µmol/mol
Argon (Ar)	300 µmol/mol
Carbon dioxide (CO_2)	2 µmol/mol
Carbon monoxide (CO) [c]	0,2 µmol/mol
Total sulfur compounds [d] (S1 equivalent)	0,004 µmol/mol
Formaldehyde (HCHO) [c]	0,2 µmol/mol
Formic acid (HCOOH) [c]	0,2 µmol/mol
Ammonia (NH_3)	0,1 µmol/mol
Halogenated compounds [e] (Halogen ion equivalent)	0,05 µmol/mol
Maximum particulate concentration [f, g]	1 mg/kg

For the constituents that are additive, such as total hydrocarbons and total sulfur compounds, the sum of the constituents shall be less than or equal to the acceptable limit.

[a] The hydrogen fuel index is determined by subtracting the "total non-hydrogen gases" in this table, expressed in mole percent, from 100 mole percent.

[b] Total hydrocarbons except methane include oxygenated organic species. Total hydrocarbons except methane shall be measured on a C1 equivalent (µmolC/mol).

[c] Sum of CO, HCHO, HCOOH shall not exceed 0.2 µmol/mol.

[d] As a minimum, total sulfur compounds include H_2S, COS, CS_2 and mercaptans, which are typically found in natural gas.

[e] Halogenated compounds include, for example, hydrogen chloride (HCl) and organic halides (R-X). Halogenated compounds shall be measured on a halogen ion equivalent (µmol/mol).

[f] Particulate includes solid and liquid particulates. Large particulates can cause issues with vehicle components and should be limited by using filter as specified in ISO19880-1 and ISO19880-8,

[g] Particulate includes oil mist. No visible oil shall be found in fuel at a nozzle.

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Fuel quality specification: PEM stationary

Constituents (assay)	Type I, grade E		
	Category 1	Category 2	Category 3
Hydrogen fuel index [a] (minimum mole fraction)	50 %	50 %	99,9 %
Total non-hydrogen gases (maximum mole fraction)	50 %	50 %	0,1%
Water (H_2O) [b]	Non-condensing at all ambient conditions	Non-condensing at all ambient conditions	Non-condensing at all ambient conditions
Maximum concentration of individual contaminants [c]			
Total hydrocarbons except methane [d] (C_1 equivalent)	10 µmol/mol	2 µmol/mol	2 µmol/mol
Methane (CH_4)	5 %	1 %	100 µmol/mol
Oxygen (O_2)	200 µmol/mol	200 µmol/mol	50 µmol/mol
Sum of nitrogen (N_2), argon (Ar) and helium (He) (mole fraction)	50 %	50 %	0,1 %
Carbon dioxide (CO_2)	Included in total non-hydrogen gases	Included in total non-hydrogen gases	2 µmol/mol
Carbon monoxide (CO)	10 µmol/mol	10 µmol/mol	0,2 µmol/mol [e]
Total sulfur compounds [f] (S1 equivalent)	0,004 µmol/mol	0,004 µmol/mol	0,004 µmol/mol
Formaldehyde (HCHO)	3,0 µmol/mol	0,2 µmol/mol	0,2 µmol/mol [e]
Formic acid (HCOOH)	10 µmol/mol	0,2 µmol/mol	0,2 µmol/mol [e]
Ammonia (NH_3)	0,1 µmol/mol	0,1 µmol/mol	0,1 µmol/mol
Halogenated compounds [g] (Halogen ion equivalent)	0,05 µmol/mol	0,05 µmol/mol	0,05 µmol/mol
Maximum particulate concentration	1 mg/kg	1 mg/kg	1 mg/kg
Maximum particle diameter	75 µm	75 µm	75 µm

NOTE For the constituents that are additive, such as total hydrocarbons and total sulfur compounds, the sum of the constituents shall be less than or equal to the acceptable limit.

a The hydrogen fuel index is determined by subtracting the "total non-hydrogen gases" in this table, expressed in mole percent, from 100 mole percent.

b Each site shall be evaluated to determine the appropriate maximum water content based on the lowest expected ambient temperature and the highest expected storage pressure.

c Maximum concentration of impurities against the total gas content shall be determined on a dry-basis.

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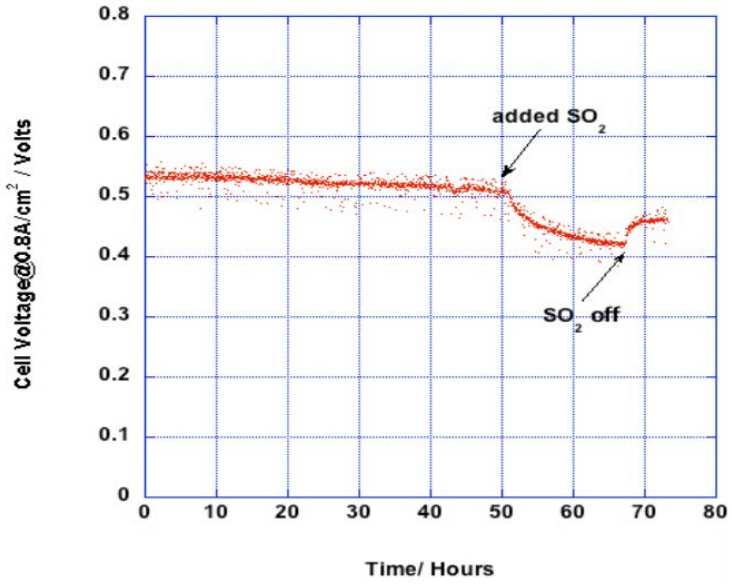
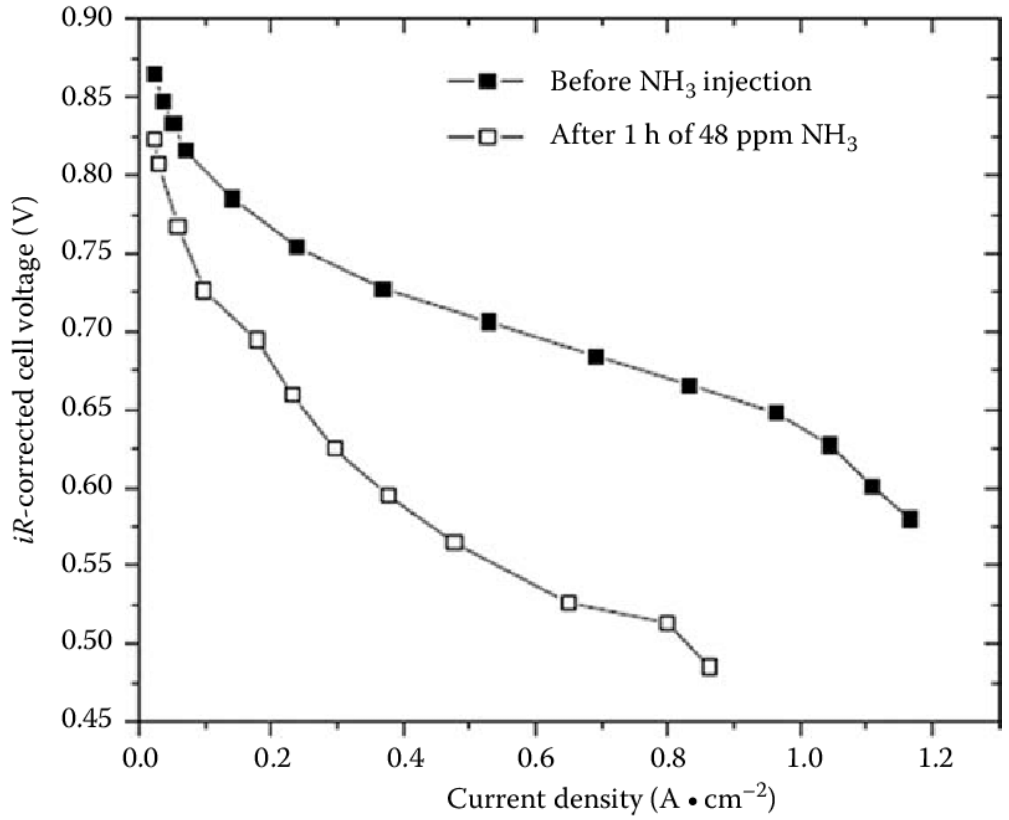
Impact of impurities

- Function of feedstock
- Dilution (N_2, Ar, He)
- Catalyst contamination (S, X, CO, HC)
- Balance of plant (inerts, CO_2, CH_4, H_2O)
- Membrane contamination (NH_3)
- Reversible and irreversible effects





Garzon, ECS Transactions 25(1) 2009

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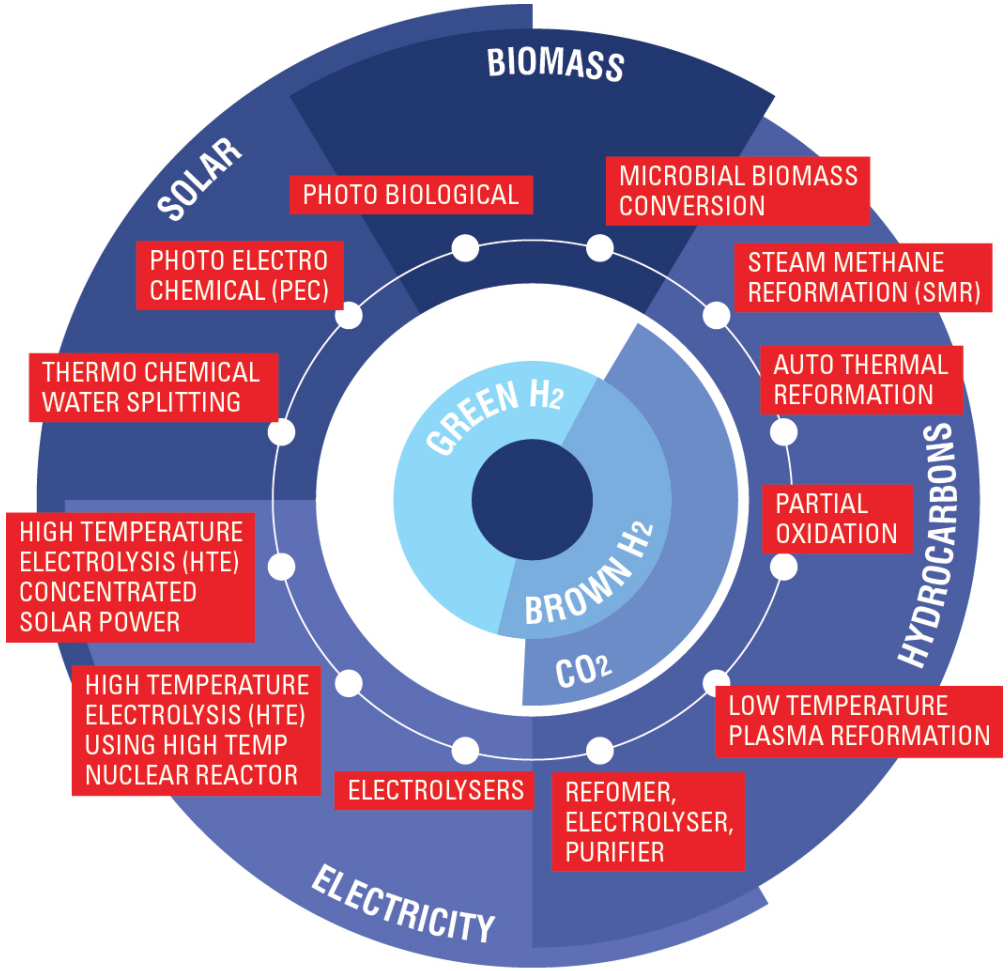
Hydrogen production



Hydrogen production types

Source	Fraction	Mt
Natural gas	.48	24
Oil/naphtha	.30	15
Coal	.18	9
Water electrolysis	0.039	2
Rest	0.001	0.005

Hydrogen composition from production

- Composition from production
- Downstream purification
- Target quality

Table 3 – Gas compositions at the outlet of the reactors for the three processes after CO_2 capture [20]

Component	Steam reforming	O_2-Blown ATR (autothermal reforming)	Coal gasification
H_2	94.3%	93.2%	87.8%
CO	0.1%	1.4%	2.6%
CO_2	2.5%	1.7%	3.9%
N_2	0.2%	0.7%	5.0%
Ar	0	0.6%	0.9%
CH_4	2.9%	2.4%	0.01%
T (°C)	33.3	35.0	30.0
P (bar a)	26.3	25.0	28.0
Q ($Nm^3 \cdot h^{-1}$)	17318	17631	19402

Besancon, IJHE 34 (2009), pp. 2350-2360

Hydrogen purification

- Adsorption augmented by
  - Pressure (PSA)
  - Temperature (TSA)
- Getter purifiers (Zr)
- (Pd) membranes
- Cryogenic

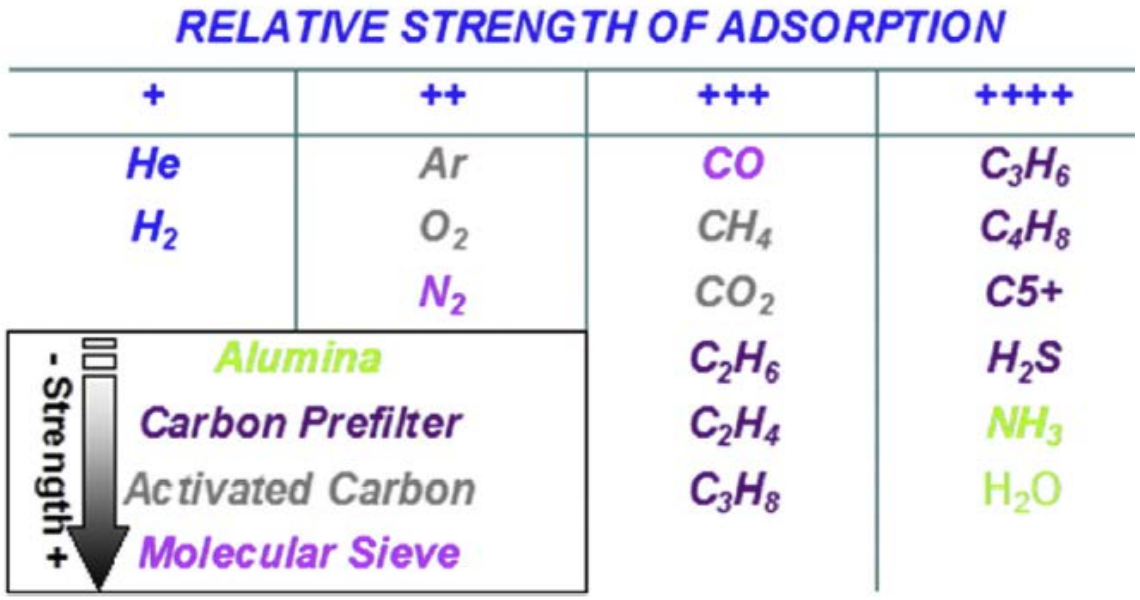


Fig. 1 – The relative strength of adsorption for gases onto the indicated adsorbents [20].

Besancon, IJHE 34 (2009), pp. 2350-2360

Hydrogen purity vs. cost

- Impurity interdependence
- Affects H_2 recovery
- QC cost driving

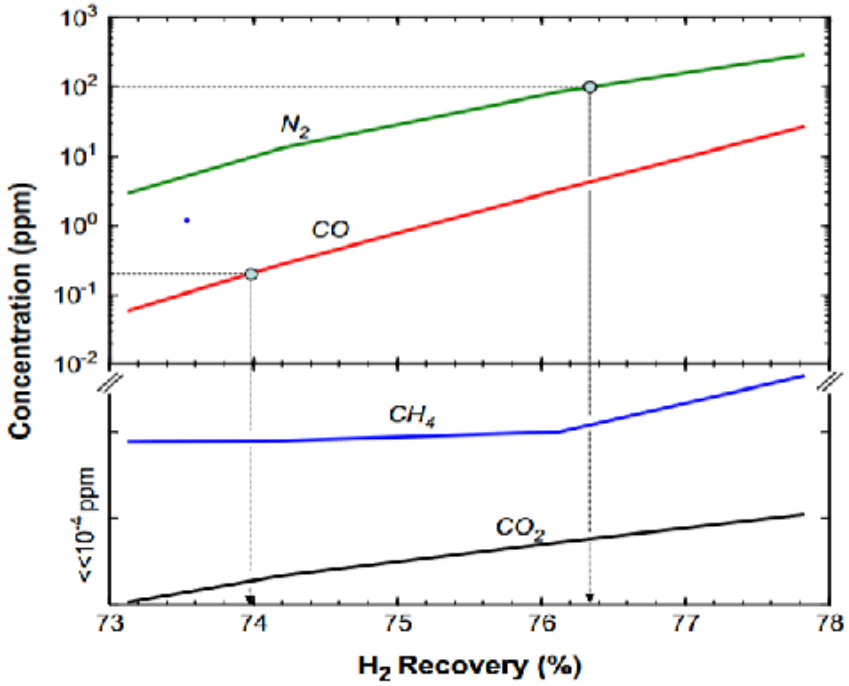


Fig. 3 – Impurity concentrations in the product hydrogen as a function of hydrogen recovery for the base-case set of conditions.

Papadias, IJHE 34 (2009) 6021–6035

Commercial hydrogen purity (HiQ example)

	2.5	4.6	5.0	6.0	5.0 Zero	7.0
Purity	99.5	99.996	99.999	99.9999	99.999	99.99999
H_2O	≤ 600	≤ 5 ppm	≤ 3	≤ 500 ppb	≤ 3 ppm	≤ 50 ppb
O_2	≤ 500	≤ 5 ppm	≤ 2	≤ 500 ppb	≤ 2 ppm	≤ 30 ppb
HC			≤ 0.5	≤ 100 ppb	≤ 200 ppb	≤ 30 ppb
N_2	≤ 3000		≤ 5	≤ 500 ppb	≤ 5 ppm	
CO				≤ 100 ppb	≤ 1 ppm	≤ 30 ppb
CO_2				≤ 100 ppb	≤ 1 ppm	≤ 30 ppb
Total impurities	5000 ppm	40 ppm	10 ppm	1 ppm	10 ppm	100 ppb

FCV fuel: 99.97%, ≤ 200 ppb CO

Commercial hydrogen purity (AIRGAS example)

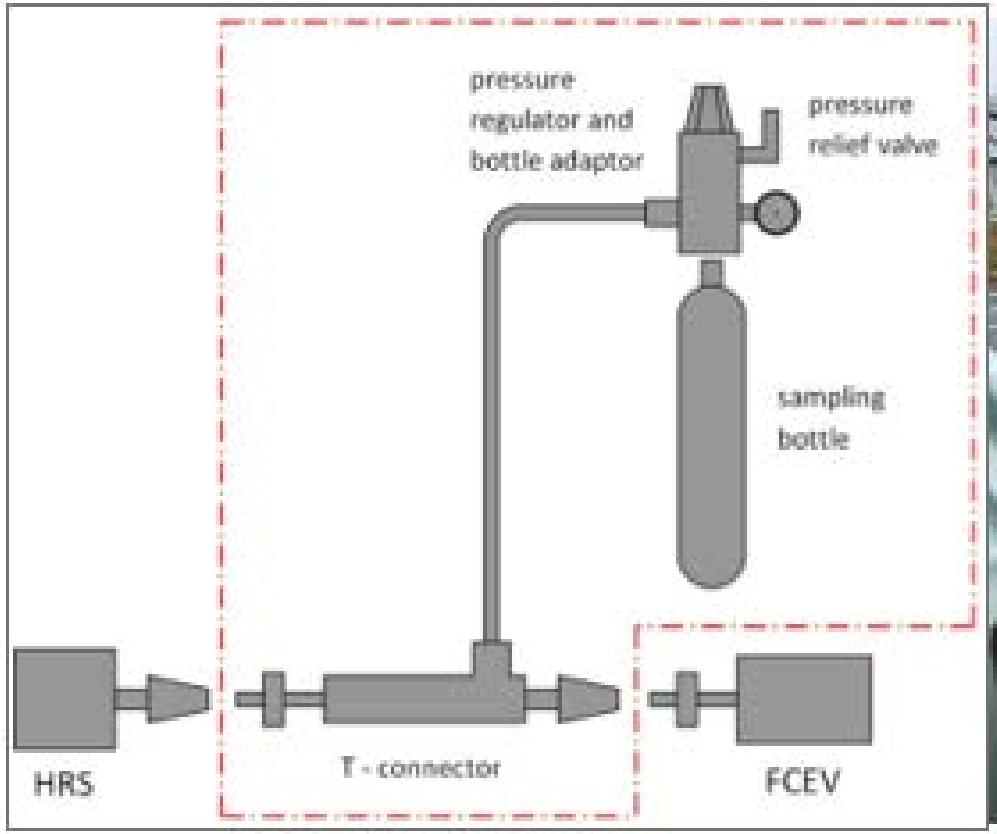
Hydrogen (H_2)

A flammable, colorless, odorless, compressed gas at high pressure.

Grade	% Purity	O2	H_2O	THC	Ar	CO	CO_2	N_2
Research[1]	99.9999	0.5	0.5	0.1	0.5	0.1	0.1	0.5
Ultra Pure Carrier	99.9995	1	1	0.5		1[2]	1[2]	3
Semiconductor[#]	99.999	1	2	0.5		1[2]	1[2]	5
Ultra High Purity	99.999	1	2	0.5		1[2]	1[2]	5
Zero Grade	99.998	5	3	0.5				
High Purity/High Pressure	99.995	4	3					
Prepurified	99.99	10	5					

Concentrations given are ppm by volume unless otherwise specified.

Sampling of hydrogen for quality control



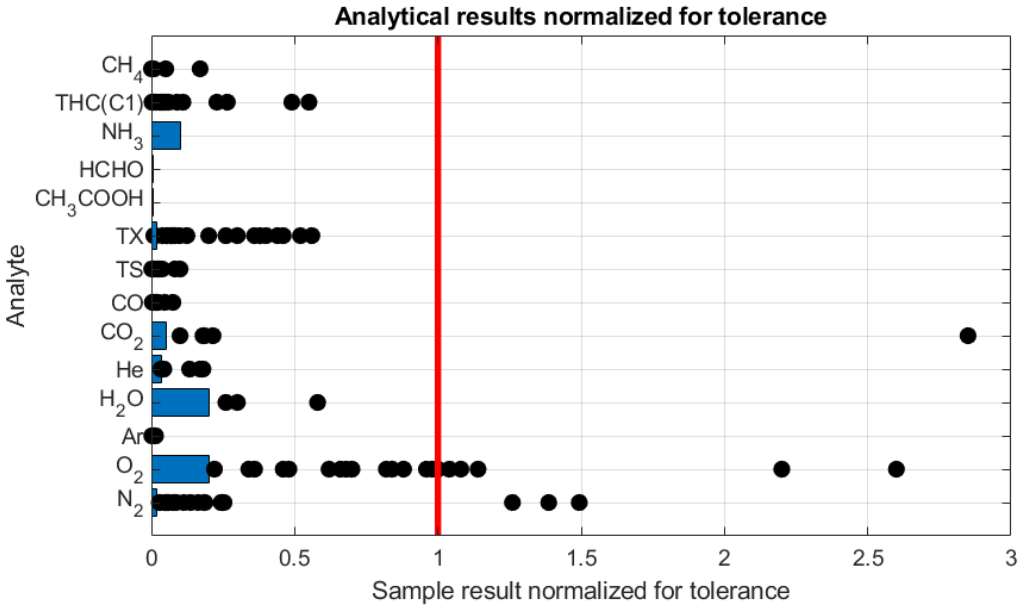
Analysis of hydrogen samples

- Comprehensive
- Expensive
- Challenging
- Need Risk Assessment to define some of the tolerance limits

Analyte	ASTM	Technique	Pre-concentration
THC (C1), HCHO, C-X	D7892	GC-MS	Cryo/TD/Cryo
He	D1946	GC-TCD	
N_2, Ar, O_2, H_2O, CO_2	D7649	GC-MS	
CO	D1946	GC-TCD	Cryo
HCO_2H, NH_3, HCl, HBr, Cl_2	WK34574(v1)	GC-ELCD	Cryo/TD/Cryo
Total sulfur	D7652	GC-SCD	Cryo/Cryo

Hydrogen purity: HyCoRA results

	N_2	O_2	Ar	H_2O	He	CO_2	CO	TS	TX	CH_3COOH	HCHO	NH_3	THC (C1)	CH_4
Tol	300	5	300	5	300	2	0,2	0,004	0,05	0,2	0,2	0,1	2	100
LOD	5	1	0,4	1	10	0,1	0,0005	0,0001	0,01	0,001	0,001	0,01	0,001	0,001
mean	131	4,58	1,24	1,90	33,6	1,21	0,003	6,7E-05	0,01	n.a.	n.a.	n.a.	1,25	1,00
mean*	32,6	3,51	1,24	1,90	33,6	0,312	0,003	6,7E-05	0,01	n.a.	n.a.	n.a.	0,19	1,00
ND	2	3	19	25	23	22	0	0	1	28	28	28	0	0
Violations	4	7	0	0	0	1	0	0	0	0	0	0	1	0
Max	1443	13	4,3	2,9	54	5,7	0,015	0,0004	0,028				30	17



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THANK YOU

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