METROLOGY for HYDROGEN VEHICLES

Analytical methods for hydrogen purity

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Workshop on hydrogen quality and flow metering for hydrogen fuel cell vehicles
11-12 September 2019, Delft (NL)

EMPIR EURAMET FCH

Overview

- What will the audience learn in this session?
- ISO/FDIS 14687 – What techniques are available?
- What parameters to consider for the analytical methods?
- Method validation / Standardised methods – status
- What is the European laboratory capability?
- Where are the next challenges?

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Hydrogen quality standards
ISO 14687 / SAE J2719 / EN 17124

	ISO 14687: 2012 / SAE J2719:2011		ISO/FDIS 14687 / EN 17124:2018	
	Max. admissible value [µmol/mol]	notes	Max. admissible value [µmol/mol]	notes
Water	5		5	
Total hydrocarbons (TC)	2	Due to CH4, TC > 2 µmol/mol	2 except CH_4	including oxygenated organic species
Methane	-		100	
Oxygen	5		5	
Helium	300		300	
Nitrogen	100	N2+Ar<100	300	
Argon	100	N2+Ar<100	300	
carbon dioxide	2		2	
Carbon monoxide	0.2		0.2	CO+HCHO+HCOOH < 0.2µmol/mol
Total sulphur compounds	0.004	H2S, COS, CS2, mercaptans (NG)	0.004	H2S, COS, CS2, 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 Cl2, organic R-X	0.05	HCl, organic R-Cl
Max. particulate conc.	1 mg/kg		1 mg/kg	

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

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Techniques

- MetroHyVe review

Family	Technique	Number of impurities	Impurities														
			Ammonia	Argon	Carbon dioxide	Carbon monoxide	Formaldehyde	Formic Acid	Halogenated compounds	Helium	Methane	Nitrogen	Non-methane hydrocarbons (NMHC)	Oxygen	Total hydrocarbons	Total sulphur compounds	Water
Number of suitable techniques per impurity			6	4	6	7	5	5	0	2	7	5	4	7	4	4	10
Gas chromatography	GC-ECD	0							Partial								
	GC-ELCD	2							Partial								
	GC-FID	3															
	GC-HID	2															
	GC-MS	6							?								
	GC-MS with jet pulse injection	7															
	GC-PDHID	6															
	GC-SCD	1															
	GC-TCD	5			LOD =												
Gas chromatography with pre-concentration	GC-FPD (with pre-concentrator)	2															
	GC-MS (with pre-concentrator)	1							Partial								
	GC-MS (with pre-concentrator) + GC-ELCD	0							Partial								
	GC-SCD (with pre-concentrator)	1															
	Methanizer GC-FID	5															
	TD-GC-FPD/MS	0														Partial	
	TD-GC-MS	1							Partial				?				
	TD-GC-MS/FID	0							Partial						LOD =		
	TD-GC-PDECD	0							Partial								
Liquid chromatography	CIC	0							Partial							?	
	DNPH-HPLC-UV-Vis DNPH-HPLC	1															
	HPLC-CD	0	LOD =														
	IC	0						?								?	
	IC with concentrator	2							Partial								
	IC-CD	1															
	Impinger - IC	0						?	?								
Spectroscopy	Continuous wave CRDS	7															
	CRDS	1															
	FTIR	7							Partial								
	OFCEAS	8							Partial							Partial	
Others	Al2O3 sensor	1															
	Chilled mirror hygrometer	1															
	Colorimetric tube	0															
	Coulimetric	1															
	EC sensor	1															
	Electrolytic hygrometer	1															
	Quartz crystal microbalance	1															
	SCD	1															

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Techniques currently tested by analytical laboratory

- No consensus or one favoured techniques

Family	Technique	Impurities															Number of impurities	Number of laboratories
		Ammonia	Argon	Carbon dioxide	Carbon monoxide	Formaldehyde	Formic acid	Halogenated compounds	Helium	Methane	Moisture	Nitrogen	Non-methane hydrocarbons	Oxygen	Total hydrocarbons	Total sulfur		
GC	GC-PDHID		3	2	3					1		2		2			6	4
	GC-MS	1	2	1		1		2	1		1	2		1			9	3
	GC-TCD		2					1	4			2					4	5
	GC-FID									2			3		2		3	3
	TD-GC-MS/FID							1							1	1	3	1
	TD-GC-MS						1	1					1				3	2
	Methanizer GC-FID			1						1					1		3	1
	GC-SCD															2	1	2
	GC-HID				1					1							2	1
	GC-FPD											1				1	2	1
	GC-ELCD	1					1										2	1
	TD-GC-PDECD							1									1	1
	TD-GC-FPD/MS															1	1	1
	GC-MS (with pre-concentrator)							1									1	1
Spectroscopy	OFCEAS	1		1	1	1					2			1		1	7	2
	FTIR	1		1	1		1	1		1							6	1
LC	IC with concentrator	1					1	1									3	1
	HPLC-CD	1															1	1
Others	Electrochemical cell													2			1	2
	Ultrathin Alumina Capacitance										1						1	1
	SCD															1	1	1
	Electrolytic Hygrometry										1						1	1
	Coulimetric													1			1	1
	Colorimetric tube	1															1	1
	Aluminium Oxide										1						1	1

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Techniques

- Large choice of techniques

Family	Technique	Number of impurities	Impurities														
			Ammonia	Argon	Carbon dioxide	Carbon monoxide	Formaldehyde	Formic Acid	Halogenated compounds	Helium	Methane	Nitrogen	Non-methane hydrocarbons (NMHC)	Oxygen	Total hydrocarbons	Total sulphur compounds	Water
Number of suitable techniques per impurity			6	4	6	7	5	5	0	2	7	5	4	7	4	4	10
Gas chromatography	GC-ECD	0							Partial								
	GC-ELCD	2							Partial								
	GC-FID	3															
	GC-HID	2															
	GC-MS	6							?								
	GC-MS with jet pulse injection	7															
	GC-PDHID	6															
	GC-SCD	1															
	GC-TCD	5			LOD =												
Gas chromatography with pre-concentration	GC-FPD (with pre-concentrator)	2															
	GC-MS (with pre-concentrator)	1							Partial								
	GC-MS (with pre-concentrator) + GC-ELCD	0							Partial								
	GC-SCD (with pre-concentrator)	1															
	Methanizer GC-FID	5															
	TD-GC-FPD/MS	0														Partial	
	TD-GC-MS	1							Partial				?				
	TD-GC-MS/FID	0							Partial						LOD =		
	TD-GC-PDECD	0							Partial								
Liquid chromatography	CIC	0							Partial							?	
	DNPH-HPLC-UV-Vis DNPH-HPLC	1															
	HPLC-CD	0	LOD =														
	IC	0						?								?	
	IC with concentrator	2							Partial								
	IC-CD	1															
	Impinger - IC	0						?	?								
Spectroscopy	Continuous wave CRDS	7															
	CRDS	1															
	FTIR	7							Partial								
	OFCEAS	8							Partial							Partial	
Others	Al2O3 sensor	1															
	Chilled mirror hygrometer	1															
	Colorimetric tube	0															
	Coulimetric	1															
	EC sensor	1															
	Electrolytic hygrometer	1															
	Quartz crystal microbalance	1															
	SCD	1															

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Techniques

One technique

Not one instrument
Or
Not the same settings

Family	Technique	Number of impurities	Impurities														
			Ammonia	Argon	Carbon dioxide	Carbon monoxide	Formaldehyde	Formic Acid	Halogenated compounds	Helium	Methane	Nitrogen	Non-methane hydrocarbons (NMHC)	Oxygen	Total hydrocarbons	Total sulphur compounds	Water
Number of suitable techniques per impurity			6	4	6	7	5	5	0	2	7	5	4	7	4	4	10
Gas chromatography	GC-ECD	0							Partial								
	GC-ELCD	2							Partial								
	GC-FID	3															
	GC-HID	2															
	GC-MS	6							?								
	GC-MS with jet pulse injection	7															
	GC-PDHID	6															
	GC-SCD	1															
	GC-TCD	5			LOD =												
Gas chromatography with pre-concentration	GC-FPD (with pre-concentrator)	2															
	GC-MS (with pre-concentrator)	1							Partial								
	GC-MS (with pre-concentrator) + GC-ELCD	0							Partial								
	GC-SCD (with pre-concentrator)	1															
	Methanizer GC-FID	5															
	TD-GC-FPD/MS	0														Partial	
	TD-GC-MS	1							Partial				?				
	TD-GC-MS/FID	0							Partial						LOD =		
	TD-GC-PDECD	0							Partial								
Liquid chromatography	CIC	0							Partial							?	
	DNPH-HPLC-UV-Vis DNPH-HPLC	1															
	HPLC-CD	0	LOD =														
	IC	0						?								?	
	IC with concentrator	2							Partial								
	IC-CD	1															
	Impinger - IC	0						?	?								
Spectroscopy	Continuous wave CRDS	7															
	CRDS	1															
	FTIR	7							Partial								
	OFCEAS	8							Partial							Partial	
Others	Al2O3 sensor	1															
	Chilled mirror hygrometer	1															
	Colorimetric tube	0															
	Coulimetric	1															
	EC sensor	1															
	Electrolytic hygrometer	1															
	Quartz crystal microbalance	1															
	SCD	1															

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Techniques

Total / Partial

What do I want to measure?

Family	Technique	Number of impurities	Impurities														
			Ammonia	Argon	Carbon dioxide	Carbon monoxide	Formaldehyde	Formic Acid	Halogenated compounds	Helium	Methane	Nitrogen	Non-methane hydrocarbons (NMHC)	Oxygen	Total hydrocarbons	Total sulphur compounds	Water
Number of suitable techniques per impurity			6	4	6	7	5	5	0	2	7	5	4	7	4	4	10
Gas chromatography	GC-ECD	0							Partial								
	GC-ELCD	2							Partial								
	GC-FID	3															
	GC-HID	2															
	GC-MS	6							?								
	GC-MS with jet pulse injection	7															
	GC-PDHID	6															
	GC-SCD	1															
	GC-TCD	5			LOD =												
Gas chromatography with pre-concentration	GC-FPD (with pre-concentrator)	2															
	GC-MS (with pre-concentrator)	1							Partial								
	GC-MS (with pre-concentrator) + GC-ELCD	0							Partial								
	GC-SCD (with pre-concentrator)	1															
	Methanizer GC-FID	5															
	TD-GC-FPD/MS	0														Partial	
	TD-GC-MS	1							Partial				?				
	TD-GC-MS/FID	0							Partial						LOD =		
	TD-GC-PDECD	0							Partial								
Liquid chromatography	CIC	0							Partial							?	
	DNPH-HPLC-UV-Vis DNPH-HPLC	1															
	HPLC-CD	0	LOD =														
	IC	0						?								?	
	IC with concentrator	2							Partial								
	IC-CD	1															
	Impinger - IC	0						?	?								
Spectroscopy	Continuous wave CRDS	7															
	CRDS	1															
	FTIR	7							Partial								
	OFCEAS	8							Partial							Partial	
Others	Al2O3 sensor	1															
	Chilled mirror hygrometer	1															
	Colorimetric tube	0															
	Coulimetric	1															
	EC sensor	1															
	Electrolytic hygrometer	1															
	Quartz crystal microbalance	1															
	SCD	1															

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Techniques

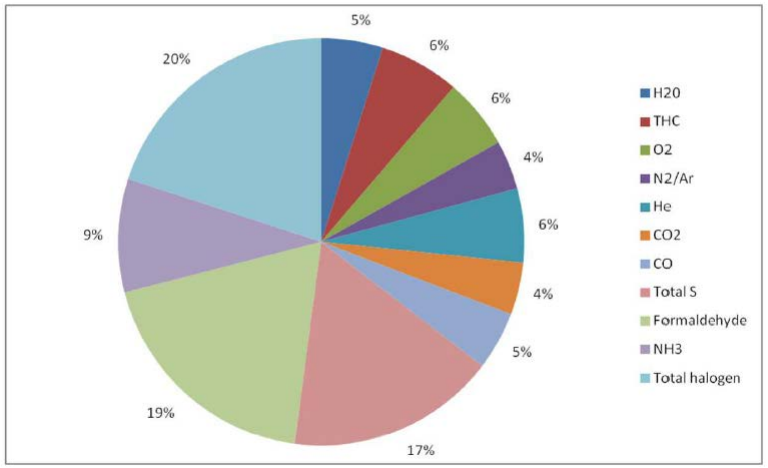
ISO 19880-8 Quality control Risk assessment

Family	Technique	Number of impurities	Impurities: Ammonia	Argon	Carbon dioxide	Carbon monoxide	Formaldehyde	Formic Acid	Halogenated compounds	Helium	Methane	Nitrogen	Non-methane hydrocarbons (NMHC)	Oxygen	Total hydrocarbons	Total sulphur compounds	Water
Number of suitable techniques per impurity			6	4	6	7	5	5	0	2	7	5	4	7	4	4	10
Gas chromatography	GC-ECD	0							Partial								
	GC-ELCD	2							Partial								
	GC-FID	3															
	GC-HID	2															
	GC-MS	6							?								
	GC-MS with jet pulse injection	7															
	GC-PDHID	6															
	GC-SCD	1															
	GC-TCD	5			LOD =												
Gas chromatography with pre-concentration	GC-FPD (with pre-concentrator)	2															
	GC-MS (with pre-concentrator)	1							Partial								
	GC-MS (with pre-concentrator) + GC-ELCD	0							Partial								
	GC-SCD (with pre-concentrator)	1															
	Methanizer GC-FID	5															
	TD-GC-FPD/MS	0														Partial	
	TD-GC-MS	1							Partial				?				
	TD-GC-MS/FID	0							Partial						LOD =		
	TD-GC-PDECD	0							Partial								
Liquid chromatography	CIC	0							Partial							?	
	DNPH-HPLC-UV-Vis DNPH-HPLC	1															
	HPLC-CD	0	LOD =														
	IC	0						?								?	
	IC with concentrator	2							Partial								
	IC-CD	1															
	Impinger - IC	0						?	?								
Spectroscopy	Continuous wave CRDS	7															
	CRDS	1															
	FTIR	7							Partial								
	OFCEAS	8							Partial							Partial	
Others	Al2O3 sensor	1															
	Chilled mirror hygrometer	1															
	Colorimetric tube	0															
	Coulimetric	1															
	EC sensor	1															
	Electrolytic hygrometer	1															
	Quartz crystal microbalance	1															
	SCD	1															

Air Liquide study

Repartition per impurities

3 impurities represent more than 50 % of the total cost



M. Carre, Quality Assurance to ensure H2 quality at HRS, HYDRAITE 1st OEM Workshop (Ulm, 07/03/2018)

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Techniques / Analytical methods

- **Techniques:** A device or a combination of **devices** used to carry out an analytical process.

- **Analytical methods:** The analytical procedure refers to the way of performing the analysis. It should **describe in detail the steps necessary to perform each analytical test**. This may include but is not limited to: the sample, the reference standard and the reagents preparations, use of the apparatus, generation of the calibration curve, use of the formulae for the calculation, uncertainty.

Impurity	Threshold in ISO 14687-2 (µmol.mol^{-1})	Limit of detection for GC-PDHID (µmol.mol^{-1})					
		NPL	CDFA-DMS	Labo 1	Labo 2	Labo 4	Labo 5
Carbon monoxide	0.2	0.012		0.05		0.02	0.1
Carbon dioxide	2	0.015		0.05		0.02	
Methane	100	0.006		0.05			
Oxygen	5	0.006			1-5		2
Nitrogen	300	0.003	11.08		1-5		100
Argon	300	0.01	11.08	0.05	1-5		100

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Analytical method selection

- What? → Defined compounds / Total family / Selection
  - Total sulphur: carbonyl sulphide, carbon disulphide, tert-butyl mercaptan, tetrahydrothiophene, methylmercaptan, H_2S
  - Total halogenated: dichloromethane, tetrachloroethylene, tetrachlorohexafluorobutane, dichlorobenzene, chloroform, HCl, HBr and Cl_2?
  - Total hydrocarbons: Methane, Ethane, propane, butanes, acetone, methanol, ethanol, octane, decane.

- How accurate?
  - Limit of detection
  - Uncertainty

- How much effort to implement?
  - Method development versus standard method
  - Method validation according to ISO 21087:2019

Total compounds

- Issue: the terminology “total” = impossible

- Analytical method has boundaries:
  - Volatility of compounds
  - Selectivity
  - Identification / Detection
  - Validation possibility (i.e. reference materials, calibrants)

- Clear boundaries on Total compounds is mandatory or expect interpretation from analytical laboratories
  - Question: Does it include any compounds reported in literature or mentioned in industry? How does the information is transferred to analytical laboratory?

Review of analytical methods

Hydrogen Contaminants	Threshold in ISO 14687-2 - EN17124 (µmol/mol)	Technique	Limit of detection (µmol/mol)	Reference
Halogenated compounds	0.05	GC-ECD	0.0001 (cannot measure non-organic halogens)	ASTM WK23815 [1]
		GC-MS (with pre-concentrator)	0.001 (only organic halogenates)	D7892-15 [2]
		TD-GC-MS	0.05 (exclusive HCl and Cl_2)	Arrhenius [3]
		GC-MS (with pre-concentrator) for organic halides + GC-ELCD for HCl, HBr and Cl_2	0.001 0.01 HBr	ASTM WK34574 [4]
		OFCEAS	0.001 (HCl only)	AP2E - manufacturer's spec [5]
		CIC	0.001 (anions, organic halogens)	ASTM D7359-18 [6], UOP 911-11 [7]
		Impinger - IC	unknown	SCAS [8]
		IC with concentrator	none stated	JIS K0127 [9]
Ammonia	0.1	FTIR	0.02	ASTM D7653-18 [10], JIS K0117 [11]
		IC-CD	None stated, 0.001 achievable	ASTM D7550-09 [12]
		HPLC-CD	0.1	Arrhenius [3]
		Continuous wave CRDS	0.00086	ASTM D7941-14 [13]
		OFCEAS	0.001	AP2E - manufacturer's spec [5]
			below 0.1	Arrhenius [3]
Formic Acid	0.2	FTIR	0.02	ASTM D7653-18 [10]
			none stated	JIS K0117 [11]
		OFCEAS	0.005	AP2E - manufacturer's spec [5]
		Impinger - IC	unknown	SCAS [8]
		IC with concentrator	0.2	Arrhenius [3]
		IC	none stated	JIS K0127 [9]
Formaldehyde	0.01	GC-MS (with pre-concentrator)	0.001	ASTM WK34574 [4]
			0.005	ASTM D7892-15 [2]
		GC-MS with jet pulse injection	0.005	ASTM D7649-10 [14]
		Continuous wave CRDS	0.0061	ASTM D7941-14 [13]
		FTIR	0.02	ASTM D7653-18 [10]
		OFCEAS	0.001	AP2E - manufacturer's spec [5]
		DNPH-HPLC-UV-Vis	0.002	Arrhenius [3]
		DNPH-HPLC	none stated	SCAS [8]

Review of analytical methods

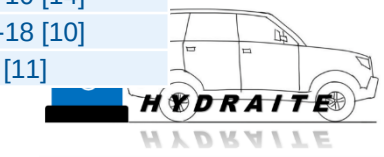
Hydrogen Contaminants	Threshold in ISO 14687-2 - EN17124 (µmol/mol)	Technique	Limit of detection (µmol/mol)	Reference
Total sulphur compounds	0.004	GC-SCD (with pre-concentrator)	0.00002	ASTM D7652-11 [15]
		GC-SCD (without pre-concentrator)	0.0014	NPL [16]
		GC-FPD (with pre-concentrator)	0.0016 - 0.0071	CDFA-DMS [17]
		OFCEAS	0.001 (H_2S only)	AP2E - manufacturer's spec [5]
			0.002 (H_2S only)	Arrhenius [3]
		IC	none stated	JIS K0127 [9]
		CIC	ppm	ASTM D7359-18 [6]
Carbon monoxide	0.2	GC-PDHID	0.012	NPL report AS 64 [18]
		Methanizer GC-FID	0.01	NPL report AS 64 [18]
		GC-TCD	0.04	NPL report AS 64 [18]
		FTIR	0.01	ASTM D7653-18 [10]
			none stated	JIS K0117 [11]
			0.02	CDFA-DMS [17]
		OFCEAS	0.001	AP2E - manufacturer's spec [5]
		Continuous wave CRDS	0.041	ASTM D7941-14 [13]
Nitrogen	300	GC-TCD	8	NPL Report AS 64 [18]
			50	Arrhenius [3]
			unknown	SCAS [8]
		GC-PDHID	0.003	NPL Report AS 64 [18]
			11.08	CDFA-DMS [17]
			none stated	JIS K0114 [19]
		GC-MS with jet pulse injection	<2.6	ASTM D7649-10 [14]
Argon	300	GC-TCD	5	NPL Report AS 64 [18]
			none stated	Arrhenius [3]
			none stated	SCAS [8]
		GC-PDHID	0.01	NPL Report AS 64 [18]
			11.08	CDFA-DMS [17]
		GC-MS with jet pulse injection	<2.6	ASTM D7649-10 [14]

Review of analytical methods

Hydrogen Contaminants	Threshold in ISO 14687-2 - EN17124 (µmol/mol)	Technique	Limit of detection (µmol/mol)	Reference
Helium	300	GC-TCD	13	NPL Report AS 64 [18]
			20	CDFA-DMS [17]
			none stated	SCAS [8]
		GC-MS	none stated	JIS K0123 [20]
Oxygen	5	EC sensor	0.3	ASTM D7607-11 [21]
		GC-MS with jet pulse injection	<2.7	ASTM D7649-10 [14]
		GC-TCD	3	NPL Report AS 64 [18]
		GC-PDHID	0.006	NPL report AS 64 [18]
		OFCEAS	1	AP2E - manufacturer's spec [5]
		Continuous wave CRDS	0.00012	ASTM D7941-14 [13]
Carbon dioxide	2	Methanizer GC-FID	0.015	NPL Report AS 64 [18]
			0.23	CDFA-DMS [17]
			none stated	SCAS [8]
		GC-PDHID	0.015	NPL report AS 64 [18]
		GC-MS with jet pulse injection	<2.7	ASTM D7649-10 [14]
			none stated	JIS K0123 [20]
		GC-TCD	2	Arrhenius [3]
		FTIR	0.01	ASTM D7653-18 [10]
			0.011	CDFA-DMS [17]
			none stated	JIS K0117 [11]
		OFCEAS	0.2	AP2E - manufacturer's spec [5]
		Continuous wave CRDS	0.161	ASTM D7941-14 [13]

Review of analytical methods

Hydrogen Contaminants	Threshold in ISO 14687-2 - EN17124 (µmol/mol)	Technique	Limit of detection (µmol/mol)	Reference
Total hydrocarbons	2	GC-FID	0.06	ASTM D7675-15 [22]
			1	Arrhenius [3]
			0.012	CDFA-DMS [17]
			none stated	JIS K0114 [19]
			none stated	SCAS [8]
		Methanizer GC-FID	0.01	NPL Report AS 64 [18]
		GC-MS	0.001 (0.002 ethane and ethene)	ASTM D7892-15 [2]
		FTIR	0.71	ASTM D7653-10 [10]
			none stated	JIS K0117 [11]
Non-methane hydrocarbons	2	Methanizer GC-FID	0.01	NPL Report AS 64 [18]
		GC-MS	0.001 (0.002 ethane and ethene)	ASTM D7892-15 [2]
Methane	100	GC-FID	0.1	CDFA-DMS [17]
		GC-PDHID	0.006	NPL report AS 64 [18]
		FTIR	0.012	CDFA-DMS [17]
		Continuous wave CRDS	0.00068	ASTM D7941-14 [13]
		OFCEAS	0.001	AP2E - manufacturer's spec [5]
Water	5	Chilled mirror hygrometer	1	Review NPL [23]
			none stated	JIS K0225 [24]
			none stated	SCAS [8]
		Quartz crystal microbalance	2	Review NPL [23]
			none stated	JIS K0225 [24]
		CRDS	0.01	NPL report AS 64 [18]
		Continuous wave CRDS	0.00008	ASTM D7941-14 [13]
		OFCEAS	0.01	AP2E - manufacturer's spec [5]
		GC-MS	0.8	NPL report AS 64 [18]
		GC-MS with jet pulse injection	<4	ASTM D7649-10 [14]
		FTIR	0.12	ASTM D7653-18 [10]
			none stated	JIS K0117 [11]



Method validation for hydrogen fuel quality

- New standard and requirement ISO 21087:2019
  - Requirements for ISO/FDIS 14687 results

- Analytical laboratory needs to comply with ISO 21087:2019
  - Inhouse analytical method
  - Standardised method: ASTM or JIS

ISO 21087:2019 - Gas analysis -- Analytical methods for hydrogen fuel -- Proton exchange membrane (PEM) fuel cell applications for road vehicles

- **Requirements for analytical method validation and fit for purpose**

  The standard defines:

  - parameters to be checked;
  - fit for purpose criteria

  The standard does not prescribe any methodology or strategy

  Validation report should be available upon request

Table 1 — Overview of characteristics for analytical methods

Performance characteristic	Clause/Subclause
Selectivity	6.2.2
Limit of detection (LOD) and limit of quantification (LOQ)	6.2.3
Working range	6.2.4
Trueness bias, recovery	6.2.5
Precision repeatability, intermediate precision and reproducibility	6.2.6
Measurement uncertainty	6.2.7
Ruggedness (robustness)	6.2.8

METROLOGY for HYDROGEN VEHICLES

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ISO 21087:2019 - Gas analysis -- Analytical methods for hydrogen fuel -- Proton exchange membrane (PEM) fuel cell applications for road vehicles

- **Requirements for analytical method validation and fit for purpose**

  The standard defines:

  - parameters to be checked;
  - fit for purpose criteria
    - Working range: LOQ + *k**LOQ < *ISO 14687 threshold < 2 * ISO 14687 threshold*
    - Limit of detection:

      k_q = 10 for specification value ≥ 1 µmol/mol

      k_q = 5 for 1 µmol/mol > specification value ≥ 10 nmol/mol

      k_q= 3 for specification value < 10 nmol/mol

      $$x_{LOQ} + u_{LOQ} < x\text{threshold}$$

      where u_{LOQ} is the uncertainty at the x_{LOQ} value. .
    - Uncertainty (including precision and bias) at the ISO threshold
      - *From micromole/mol to 10 nmol/mol* → *Relative uncertainty < 10%*
      - *Below 10 nmol/mol* → *Relative uncertainty < 50%*

Validation report should be available upon request

METROLOGY for HYDROGEN VEHICLES

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Method validation for hydrogen fuel quality

- Method validation following ISO 21087:2019
  - Requirements for ISO/FDIS 14687 results

- Standardised method: ASTM or JIS
  - Clear procedure applied to hydrogen fuel
    - ASTM D7652 – 11 -Standard Test Method for Determination of Trace Hydrogen Sulfide, Carbonyl Sulfide, Methyl Mercaptan, Carbon Disulfide and Total Sulfur in Hydrogen Fuel by Gas Chromatography and Sulfur Chemiluminescence Detection
    - JIS K0123 – General rules for gas chromatography / Mass spectrometry

  Fit for purpose?

  - Standard method need to comply with ISO 21087:2019
    - 13.2 *Reproducibility*—The reproducibility of this test method for measuring impurities present in H2 fuel gas, is being determined and will be available within five years of the publication of this standard, based upon the results of interlaboratory testing.
    - 13.3 *Bias*—The bias for each component analyzed will be determined by experimental results within five years of the release of this standard.

  Comply with ISO 21087 criteria?

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New analytical methods for reactive compounds - MetroHyVe

- **VSL: Analytical method using mid-infrared CRDS spectrometer**
  - Formic acid: Working range: 20 nmol/mol –10 µmol/mol
  - Formaldehyde: Working range: 7 nmol/mol –20 µmol/mol
  - HCl: Working range: 1.5 nmol/mol –50 µmol/mol
  - Use of passivated system and dynamically generated standards

- **RISE: TD-GC-MS (Tenax TA / Carboxen 1003 / Carbograph 1)**
  - Halogenated compounds: chloroform, dichloromethane, tetrachloroethylene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 2,2,3,3-tetrachlorofluorobutane, 1,2,3,4-tetrachlorofluorobutane, 1,1,3,4-tetrachlorofluorobutane.

METROLOGY for HYDROGEN VEHICLES

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European analytical laboratories: RISE

Hydrogen contaminant	Threshold in ISO 14687-2	Limit of detection	Technique
Moisture	5 µmol/mol	0.05	OFCEAS
Oxygen	5 µmol/mol	1	OFCEAS
Carbon monoxide	0.2 µmol/mol	0.002	OFCEAS
Total sulphur	0.004 µmol/mol		
H2S	Subset of TS	0.001	OFCEAS
Mercaptans	Subset of TS	0.005	TD-GC/MS-FID
Thiophenes	Subset of TS	0.005	
Nitrogen	300 µmol/mol	30	GC/TCD
Halogenated compounds	0.05 µmol/mol		
organic halogenated compounds	Subset of T-X	0.01	TD-GC/MS-FID
Formic acid	0.2 µmol/mol		
Formaldehyde	0.2 µmol/mol		
Argon	300 µmol/mol	30	GC/TCD
Helium	300 µmol/mol		
Carbon dioxide	2 µmol/mol	0.2	OFCEAS
Total hydrocarbons	2 µmol/mol	2	GC/FID+TD-GC/MS-FID
Non-methane hydrocarbons	2 µmol/mol	1	
alkohol (methanol, ethanol…)	Subset of Total hydrocarbons	1	GC/FID
Ketones (acetone…)	Subset of Total hydrocarbons	1	GC/FID
Methane	100 µmol/mol	0.04	GC/FID
Ammonia	0.1 µmol/mol	0.1	HPLC/Conductivity detector

European analytical laboratories: Air Liquide

Hydrogen contaminant	Threshold in ISO 14687-2	Limit of detection	Technique
Moisture	5 µmol/mol	0.5	OFCEAS
Oxygen	5 µmol/mol	2	GC-PDHID
Carbon monoxide	0.2 µmol/mol	0.1	GC-PDHID
Total sulphur	0.004 µmol/mol	See below	-
Methyl mercaptans	Subset of TS	0.001	TD-GC-FPD/MS
Carbonyl sulphide	Subset of TS	0.001	TD-GC-FPD/MS
Hydrogen sulphide	Subset of TS	0.001	TD-GC-FPD/MS
Carbon disulphide	Subset of TS	0.001	TD-GC-FPD/MS
Nitrogen	300 µmol/mol	10	GC-PDHID
Halogenated compounds	0.05 µmol/mol	See below	-
Dichloromethane	Subset of T-X	0.02	TD-GC-PDECD
Formic acid	0.2 µmol/mol	0.1	TD-GC-MS
Formaldehyde	0.2 µmol/mol	0.02	OFCEAS
Argon	300 µmol/mol	10	GC-PDHID
Helium	300 µmol/mol	10	GC-TCD
Carbon dioxide	2 µmol/mol	0.2	GC FID methaniser
Total hydrocarbons	2 µmol/mol	0.2	GC FID methaniser
Non-methane hydrocarbons	2 µmol/mol	-	-
Acetylene	Subset of Total hydrocarbons		TD-GC-MS
Ethylene	Subset of Total hydrocarbons		TD-GC-MS
Ethane	Subset of Total hydrocarbons		TD-GC-MS
Propene	Subset of Total hydrocarbons		TD-GC-MS
Propane	Subset of Total hydrocarbons		TD-GC-MS
Methane	100 µmol/mol	0.2	GC FID methaniser
Ammonia	0.1 µmol/mol	0.03	OFCEAS

European analytical laboratories: VSL

Hydrogen contaminant	Threshold in ISO 14687-2	Limit of detection	Technique
Moisture	5 µmol/mol	0.02	CRDS
Oxygen	5 µmol/mol	5	GC-TCD
Carbon monoxide	0.2 µmol/mol	1	CRDS
Total sulphur	0.004 µmol/mol	0.002	GC-SCD
Halogenated compounds	0.05 µmol/mol	0.0005 (HCl)	CRDS
Formic acid	0.2 µmol/mol	0.007	CRDS
Formaldehyde	0.2 µmol/mol	0.002	CRDS
Carbon dioxide	2 µmol/mol	0.01	CRDS
Total hydrocarbons	2 µmol/mol	0.5	GC-PDHID
Non-methane hydrocarbons	2 µmol/mol	0.5	GC-PDHID
Methane	100 µmol/mol	0.001	CRDS
Ammonia	0.1 µmol/mol	0.1	CRDS

European analytical laboratories: ZBT

Contaminant	ISO/FDIS 14687 / EN 17124:2018	Analytical Method	Detection Limit
	[µmol/mol]		[µmol/mol]
Water	5	Quartz crystal microbalance IMR-MS	0.1 3.044**
Total Hydrocarbons	2	GC-PED IMR-MS	0.01 0.0105*
Methane	100	GC-PED IMR-MS	0.01 0.0117*
Oxygen	5	GC-PED IMR-MS	0.01 0.209*
Helium	300	EI-MS	0.0041*
Argon	300	GC-PED EI-MS	0.05 0.00039*
Nitrogen	300	GC-PED EI-MS	0.1 0.01*
Carbon Dioxide	2	IMR-MS	0.987**
Carbon Monoxide	0.2	GC-PED IMR-MS	0.001 0.06**
Total sulphur compounds	0.004	TD-GC-SCD IMR-MS	< 0.001 0.0009 (H_2S)*
Formaldehyde	0.2	IMR-MS	0.0015*
Formic Acid	0.2	IMR-MS	0.0039*
Ammonia	0.1	IMR-MS	0.0018*
Key halogenated compounds	0.05	IMR-MS	< 0.067**

METROLOGY for HYDROGEN VEHICLES

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European analytical laboratories: ZSW

Contaminant	ISO/FDIS 14687 EN17124:2018	Analytical Method	Lower Quantification Limit	estimated amount of gas needed
	µmol/mol		[µmol/mol]	[L]
Water	5	Dew Point mirror	< 1*	45
Total Hydrocarbons	2	(GC)-FID	< 0.05*	16
Methane	100	GC-PDHID	< 0.1*	16
Oxygen	5	GC-PDHID	< 0.1*	16
Oxygen	5	GC-TCD	< 5*	6
Helium	300	GC-TCD	10*	6
Argon	300	GC-PDHID	0.1*	16
Argon	300	GC-TCD	< 2.5*	6
Nitrogen	300	GC-PDHID	< 0.1*	16
Nitrogen	300	GC-TCD	10	6
Carbon Dioxide	2	GC-PDHID	< 0.9*	13.6
Carbon Monoxide	0.2	GC-PDHID	< 0.1*	16
Carbon Monoxide	0.2	OFCEAS	0.003**	10
Total sulphur compounds	0.004	TD-(GC-)FPD	0.001 (< 0.001)***	1.2
Formaldehyde	0.2	OFCEAS	0.003**	10
Formic Acid	0.2	OFCEAS	0.003**	10
Ammonia	0.1	OFCEAS	0.01**	10
Halogenated compounds	0.05	TD-(GC-)ECD	< 0.005***	16

European analytical laboratories: NPL

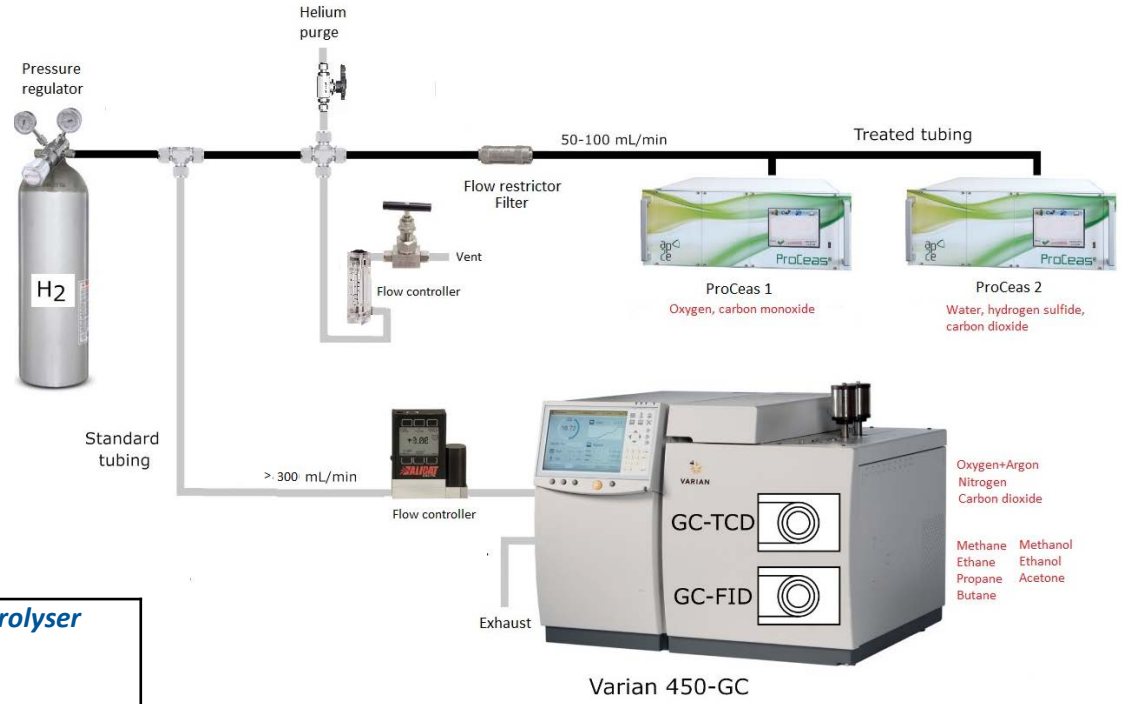
Contaminant	ISO/FDIS 14687 / EN 17124 :2018	Analytical Method	Detection Limit	Required amount of gas
	[µmol/mol]		[µmol/mol]	[L]
Water	5	Quartz crystal microbalance CRDS	0.2 0.030	30 30 - 60
Total Hydrocarbons	2	GC-Methaniser-FID	0.05	2
Methane	100	GC-Methaniser-FID	0.05	2
Oxygen	5	GC-PDHID	0.3	2
Helium	300	GC-TCD	10	2
Argon Nitrogen	300	GC-PDHID	0.3 1	2
Carbon Dioxide	2	GC-Methaniser-FID	0.02	2
Carbon Monoxide	0.2	GC-Methaniser-FID	0.02	2
Total sulphur compounds	0.004	GC-SCD	0.001	1
Formaldehyde	0.2	GC-Methaniser-FID SIFT-MS	0.05 0.02	2 2
Formic Acid	0.2	FTIR SIFT-MS	0.05 0.02	30 2
Ammonia	0.1	FTIR SIFT-MS	0.05 0.02	30 2
Key halogenated compounds according to ASTM D7892-15	0.05	TD-GC-MS	0.016	1.5

MetroHyVe - Cost efficient analyser – Dedicated scope

ISO 19880-8 Quality control

Risk assessment

- CAPEX reduction > 30% (compare 500k€ estimation)
- Optimisation of OPEX (1 hour / sample)



Probability of impurity presence	***Steam methane reforming with PSA***	***Chlor-alkali process (membrane cell process)***	***PEM water electrolysis process with TSA***	***Alkaline electrolyser***
Frequent	*CO*	*O_2*	*None identified*	*None identified*
Possible	*N_2*	*None identified*	*None identified*	*N_2*
Rare	*CH_4, H_2O and Ar*	*N_2 and H_2O*	*N_2, O_2 and H_2O*	*O_2, H_2O*
Very rare	*CH_2O*	*CO_2*	*CO_2*	*Ar*
Unlikely	*He, CO_2, O_2, CH_2O_2, NH_3, Sulphur compounds, hydrocarbons compounds, halogenated compounds*	*He, Ar, CO, CH_4, CH_2O, CH_2O_2, NH_3, Sulphur compounds, hydrocarbons compounds, halogenated compounds*	*He, Ar, CO, CH_4, CH_2O, CH_2O_2, NH_3, Sulphur compounds, hydrocarbons compounds, halogenated compounds*	*CO_2, CO, CH_4, Sulphur compounds, NH_3, hydrocarbons compounds, halogenated compounds, CH_2O, CH_2O_2, He*

METROLOGY for HYDROGEN VEHICLES

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Analytical methods summary

- Multiple techniques and analytical methods potentially applicable
  - MetroHyVe review available soon
- Define your measurand (especially for total compounds)
- Compliance with ISO 21087:2019
  - Validation for standard method if all criteria not covered
  - Measurement reported with uncertainty and validation report available
- European analytical laboratories
  - Competence for ISO 14687 and EN 17124:2018
  - Getting compliant to ISO 21087
- Benefit for reduced scope – Reduce CAPEX and OPEX

New challenges

- Compliance with ISO 21087:2019
  - Technical requirement / criteria to be met

- Quality control
  - Reference materials
  - Inter-comparison
- Gas calibrants

  Availability of gas standards for all contaminants with suitable uncertainty

- Revision of total terminology – standardisation committee?

Available resources

- MetroHyVe - *A4.3.1: Review and selection of compounds for total measurements (halogenated, sulphur and hydrocarbons)*
- ISO 21087:2019
- https://hydraite.eu/1st-hydraite-workshop/
- https://www.metrohyve.eu/downloads/

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No 779475. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme and Hydrogen Europe and Hydrogen Europe Research.

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

THANK YOU

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