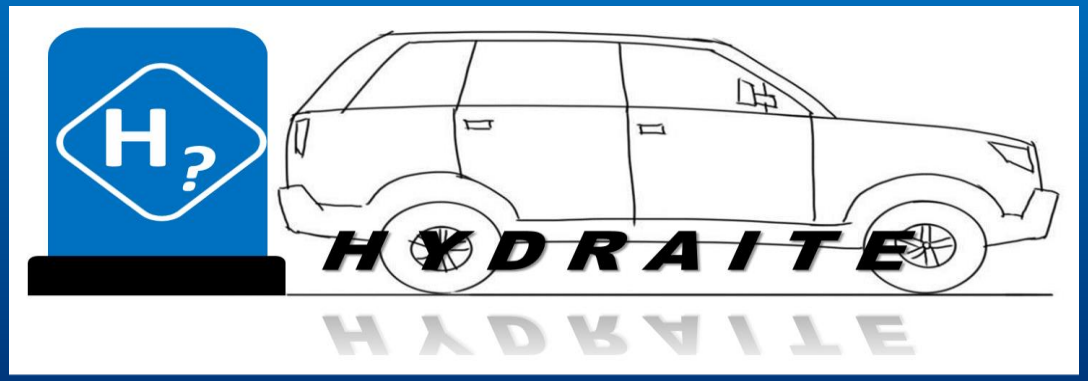

Existing normative documents about hydrogen quality and their challenges regarding gas analytics

HYDRAITE 1st OEM workshop
March 7 and 8, 2018 – Ulm/Germany

Thomas Bacquart – Higher Research Scientist - NPL
Arul Murugan – Senior Research Scientist - NPL

- Existing normative documents
- Challenges
- Normative documents evolution
- HYDRAITE project

Existing normative documents for fuel cell vehicles

Hydrogen Fuel Quality for Fuel Cell Vehicles	SAE J2719:2011	List of contaminants
Quality characteristics of hydrogen fuel for transport applications	ISO 14687-2: 2012 → ISO/CD 14687 (Approved for registration as DIS)	List of contaminants Nozzle sample
Fuel quality control	ISO/DIS 19880-8	Nozzle and other locations Risk assessment “Level 1” value Routine analysis
Hydrogen fuel - Product specification and quality assurance	prEN 17124:2017	List of contaminants Nozzle and other locations Risk assessment “Level 1” value Routine analysis

Technical challenges linked to ISO 14687

	ISO 14687: 2012 / SAE J2719:2011		ISO/CD 14687 / EN 17124	
	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	

Technical challenges linked to ISO 14687

Multiple compounds

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Low amount fraction

Technical challenges linked to ISO 14687

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Max. particulate conc.	1 mg/kg		1 mg/kg	

Unstable compounds

Low amount fraction

Challenges: interpretation of "total"

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	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**
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Max. particulate conc.	1 mg/kg		1 mg/kg	

Analytical challenges: Total compounds and halogenated

- Challenges: interpretation of terminology total

- Halogenated / sulphur / hydrocarbons: large number of molecules

- Analysis of total: volatile, key species, water soluble
  - "Total" volatile halogenated: Gas chromatography with specific detector
  - Specific compounds: ASTM D7892-15 (36 compounds)
  - Water soluble halogenated: Ion chromatography and preconcentrator

Equivalent?

What should we measure? What is the equivalence or difference?

Analytical challenges: Total compounds and halogenated

	ISO/CD 14687 / EN 17124		MetroHyve project
	Maximum admissible value [µmol/mol]	notes	List of compounds selected
Total hydrocarbons except methane	2	including oxygenated organic species	Methane, Ethane, propane, butanes, acetone, methanol, ethanol, octane, decane.
Total sulphur compounds	0.004	H_2S, COS, CS_2, mercaptans (found in natural gas)	H_2S, COS, CS_2, tert-butyl mercaptan, tetrahydrothiophene, methylmercaptan
Halogenated compounds	0.05	HCl, organic R-Cl	HCl, dichloromethane, tetrachloroethylene, tetrachlorohexafluorobutane, dichlorobenzene, chloroform

Gas analysis: Which solutions is suitable?
What is the understanding behind total?

Technical challenges linked to ISO 14687 (1)

Multiple compounds

	ISO 14687: 2012 / SAE J2719:2011		ISO/CD 14687 / EN 17124	
	Max. admissible value [µmol/mol]	notes	Max. admissible value [µmol/mol]	notes
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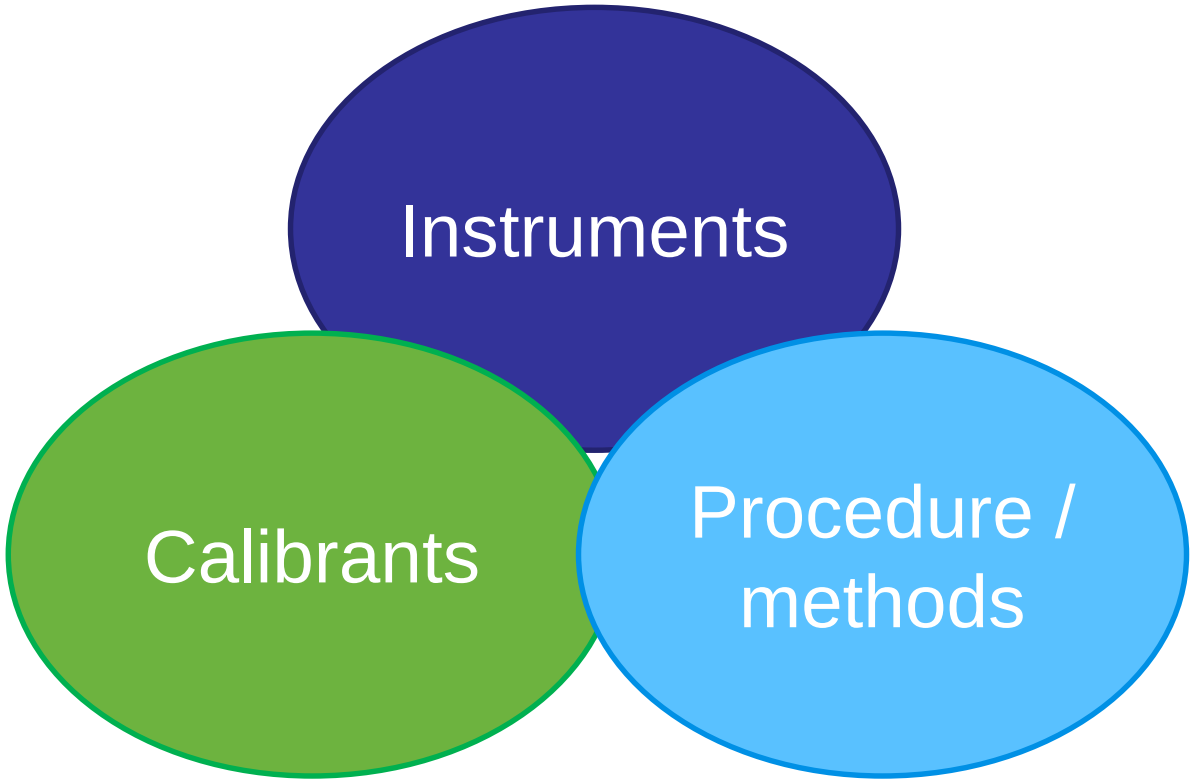
Max. particulate conc.	1 mg/kg		1 mg/kg	

Unstable compounds

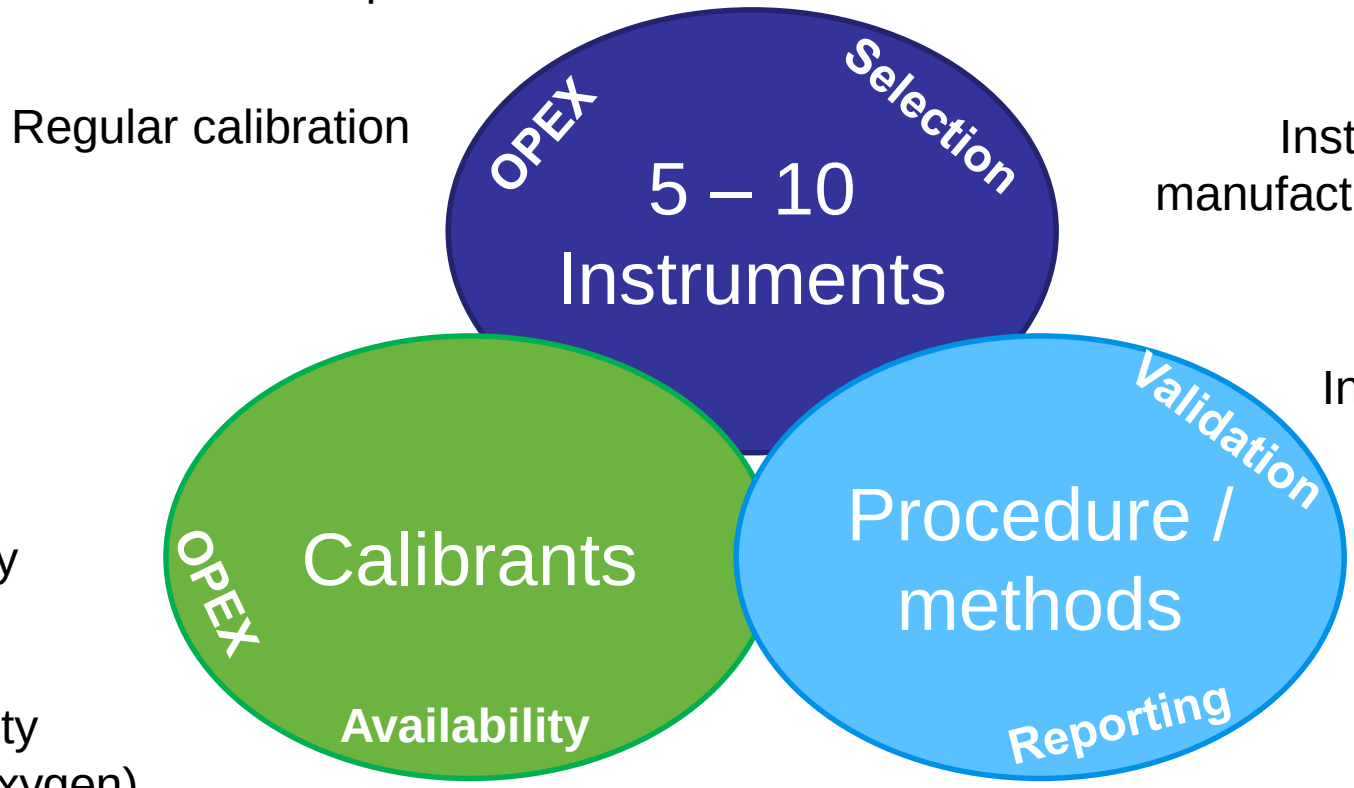
Low amount fraction

Technical challenges linked to ISO 14687 (2)

Analytical laboratory



Technical challenges linked to ISO 14687 (3)



Experienced staff to operate

Complex analytical instruments (i.e. TD-GC-MS, IMR-MS, TD-GC-FPD)

Regular calibration

Instruments manufacturer validation

International standards on methods (ASTM, JIS)

Gas calibrants availability

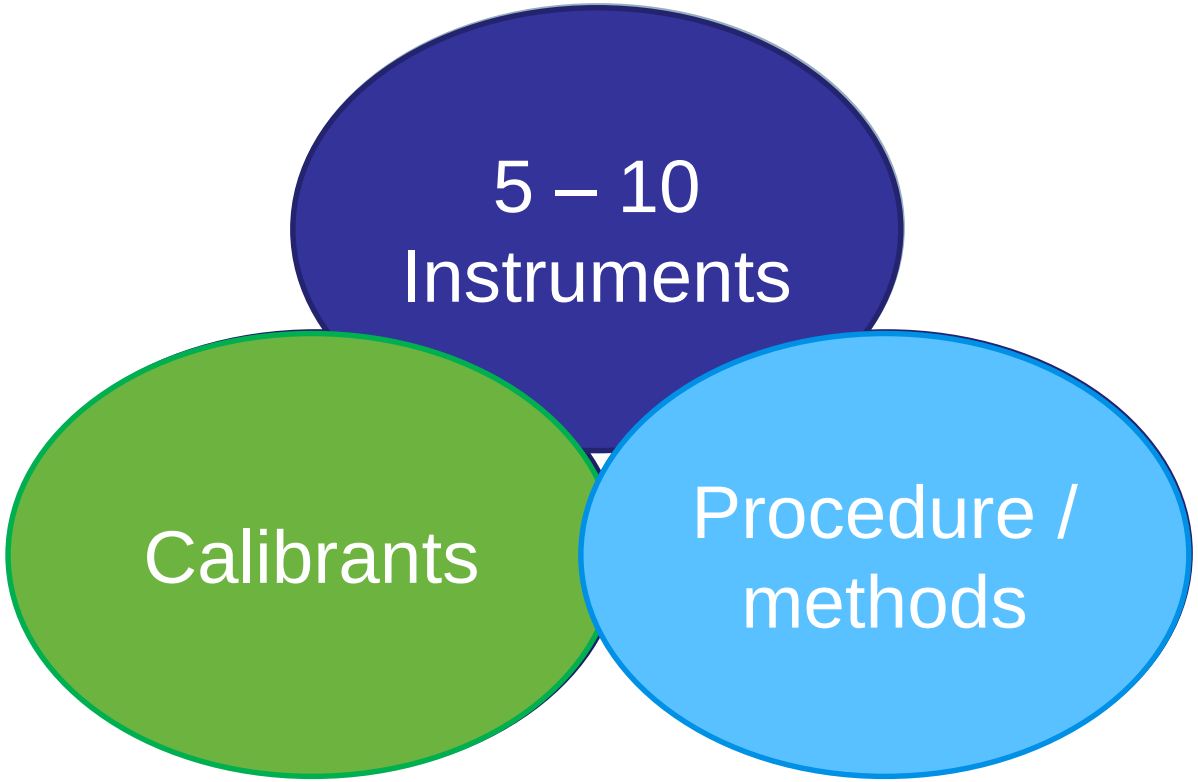
ISO/CD 21087

Gas calibrants stability (i.e. formaldehyde, oxygen)

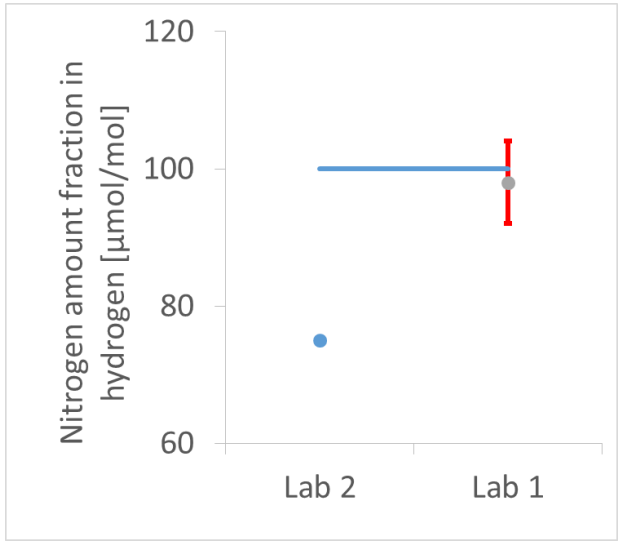
Uncertainty

Dynamic gas calibrants

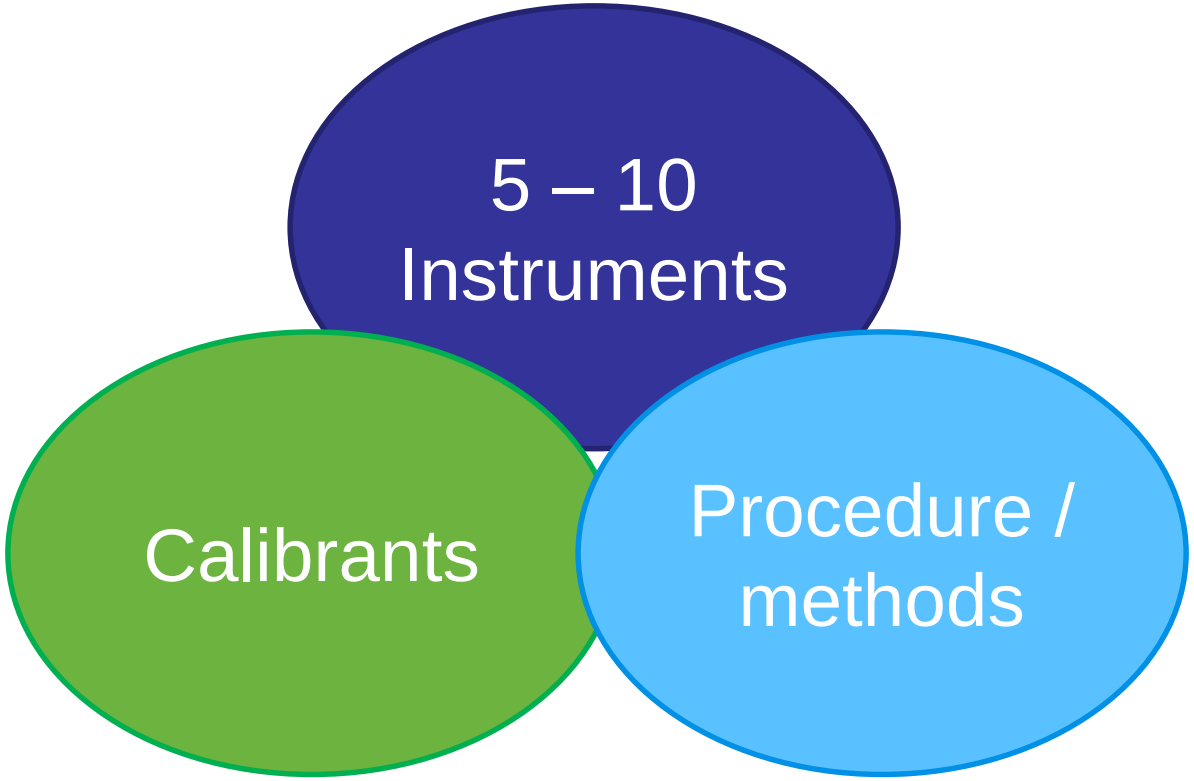
True value and uncertainty



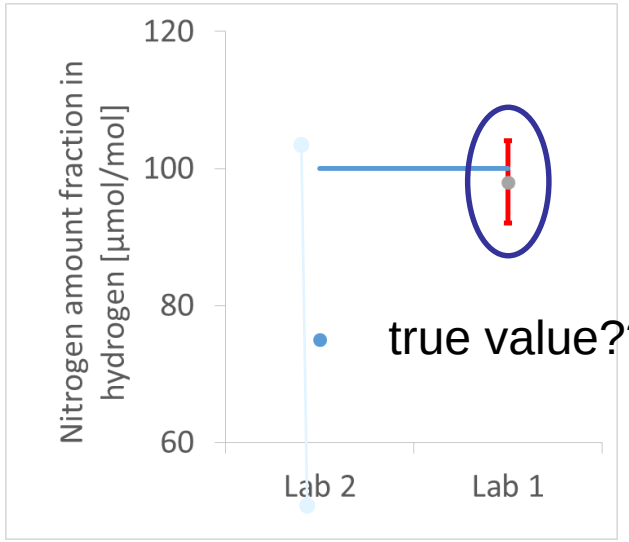
Average value and uncertainty



True value and uncertainty



Average value and uncertainty



95 % confidence: true value

true value????: threshold???

Average value without uncertainty ≠ information on compliance

ISO/CD 21087: expanded uncertainty < 20 % (*k*=2)

Inter-comparison

Analytical laboratory

Instruments

Calibrants

Procedure / methods

Results 1 ± x (*k*=2)

Analytical laboratory

Instruments

Calibrants

Procedure / methods

Results 2 ± x (*k*=2)

Analytical laboratory

Instruments

Calibrants

Procedure / methods

Results 3 ± x (*k*=2)

Equivalent or Different

Inter-comparison exercises (Hydraite, MetroHyve, Hy-Lab)

From ISO 14687-2:2012 and SAE J2719:2011 to ISO/CD 14687 and prEN 17124

	ISO 14687-2:2012 / SAE J2719:2011		ISO/CD 14687 / prEN 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	N2+Ar<100	**300**	
Argon	100	N2+Ar<100	**300**	
carbon dioxide	2		2	
Carbon monoxide	0.2		0.2	**CO+HCHO+HCOOH < 0.2 µmol/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 < 0.2 µmol/mol**
Formic acid	0.2		0.2	**CO+HCHO+HCOOH < 0.2 µmol/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	

Normative documents evolution: Quality control standard: ISO 19880-8

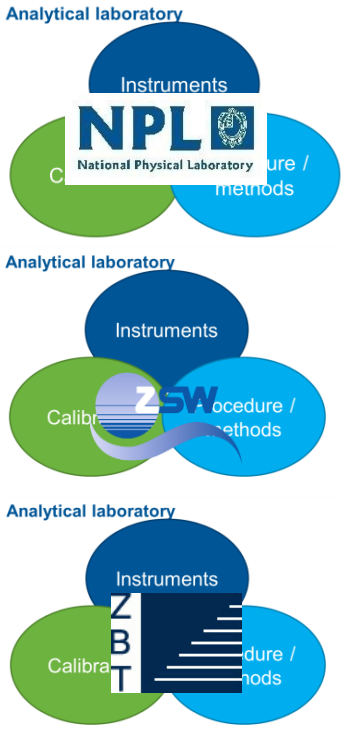
- ISO 19880-8: Fuel quality control
- Quality control:
  - prescriptive approach
  - Risk assessment
- Quality control plan:
  - Frequency;
  - list of key contaminants.
- Value 1: implication for analysis range and calibration

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	1[3]	300[3]	4
Oxygen	O2	0	5	No test data available	No test data available	Without test data for proposed level 1 value validation already SC4 if ISO Spec exceeded
Carbon dioxide	CO_2	0	2	1	3	4
Carbon monoxide	CO	0-2	0,2	2-3[4]	1	4
Methane	CH_4	0	100	1	300	4
Water	H_2O	0	5	4	NA	Already SC4 if ISO Spec exceeded
Total sulfur compounds	H_2S basis	0-4	0.004	4	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[4]	NA	Already SC4 if ISO Spec exceeded
Formaldehyde	CH_2O	0	0.01	2-3[4]	1	4
Formic Acid	CH_2O_2	0-2	0.2	2-3[4]	1	4
Total halogenated compounds		0-4	0.05	4	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

HYDRAITE – Establishing expert hydrogen purity laboratories

3 independent laboratories capable ISO 14687

ISO/CD 14687



Method validation: guidelines of ISO/CD 21087 uncertainty budget

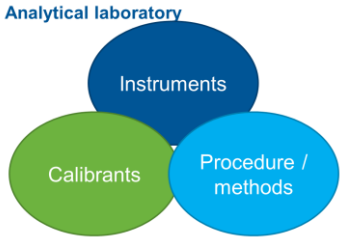
HYDRAITE – Establishing expert hydrogen purity laboratories

3 independent laboratories capable ISO 14687

ISO/CD 14687

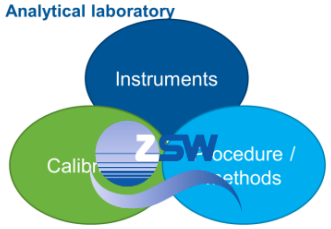
Reference laboratory of HYCORA project

N = 30 samples (HYDRAITE project) + International inter-comparison

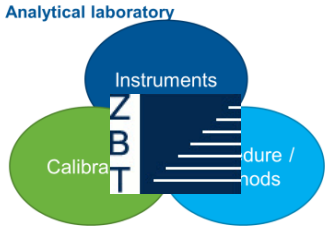


Results ref HYCORA ± x (*k*=2)

Results 1 ± x (*k*=2)



Results 2 ± x (*k*=2)



Results 3 ± x (*k*=2)

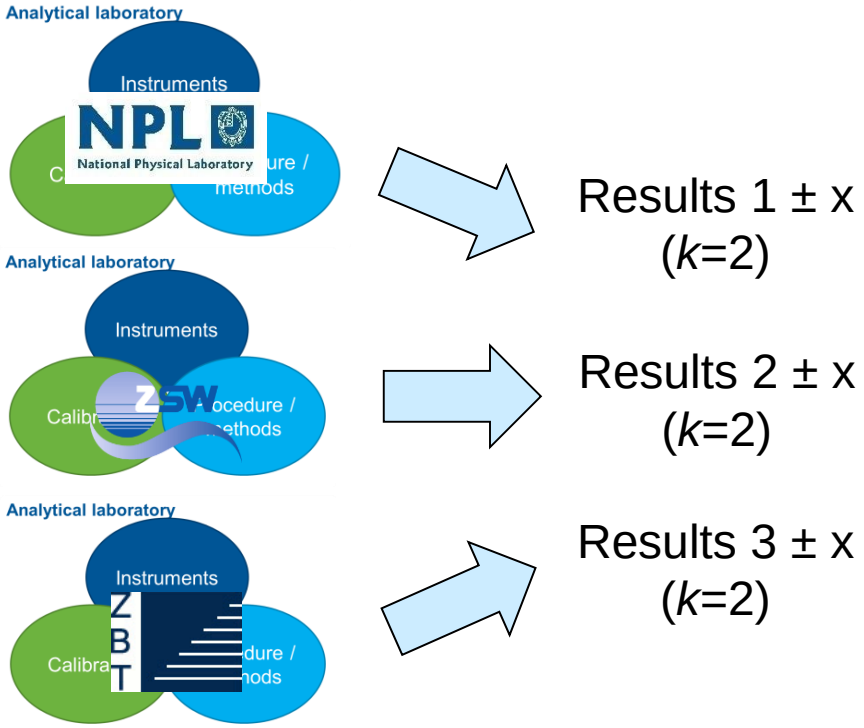
Understand agreement and disagreement

HYDRAITE – Establishing expert hydrogen purity laboratories

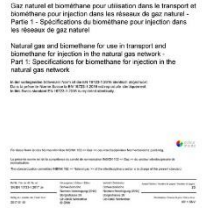
3 independent laboratories capable ISO 14687

ISO/CD 14687

Inter-comparison including sampling



HYDRAITE – Establishing expert hydrogen purity laboratories



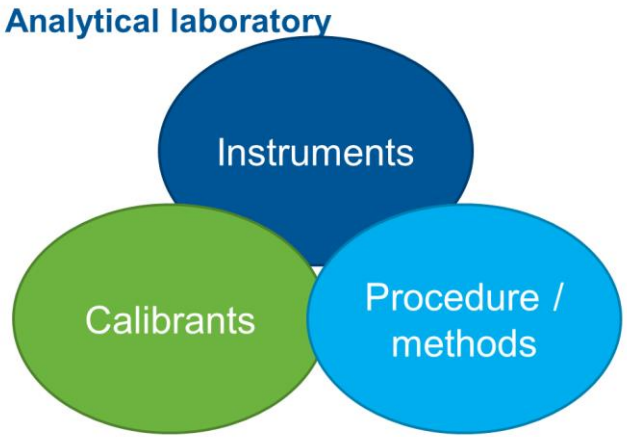
New regulation / New compounds

Experimental evidences

Sampling

- Reliable
- High pressure
- Stability

How to sample new contaminants?

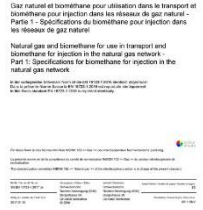


Do we have instruments?

Do we have calibrants?

Do we have methods?

HYDRAITE – Establishing expert hydrogen purity laboratories



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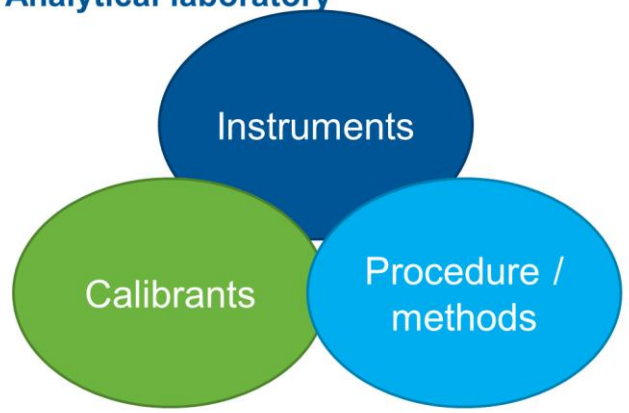
Analytical laboratory



Do we have instruments?

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Do we have methods?

We need your feedback

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.

Thank you for your attention

thomas.bacquart@npl.co.uk