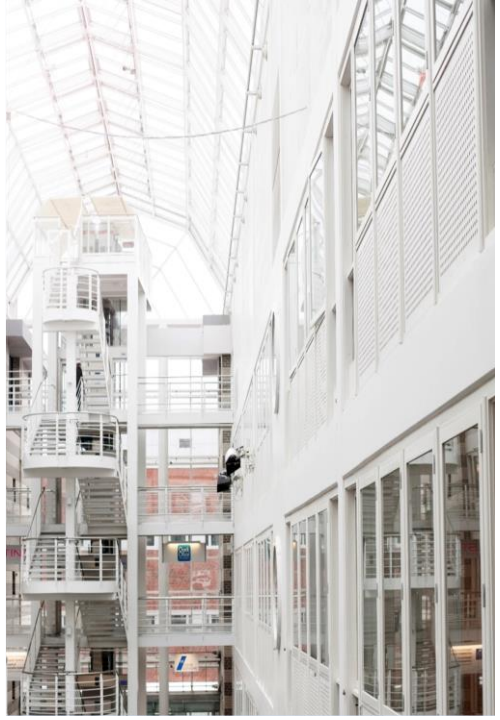
INTERNATIONAL WORKSHOP

METROLOGY FOR SUSTAINABLE HYDROGEN ENERGY APPLICATIONS

7 –8 NOVEMBER 2018

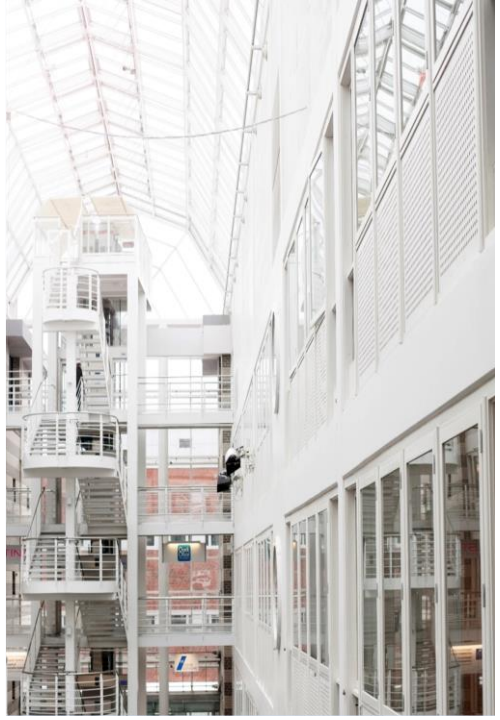
ANALYTICAL METHODS REVIEW FOR HYDROGEN QUALITY CONTROL ACCORDING TO ISO STANDARDS

Oliver Büker (RISE) / Martine Carré (Air Liquide)

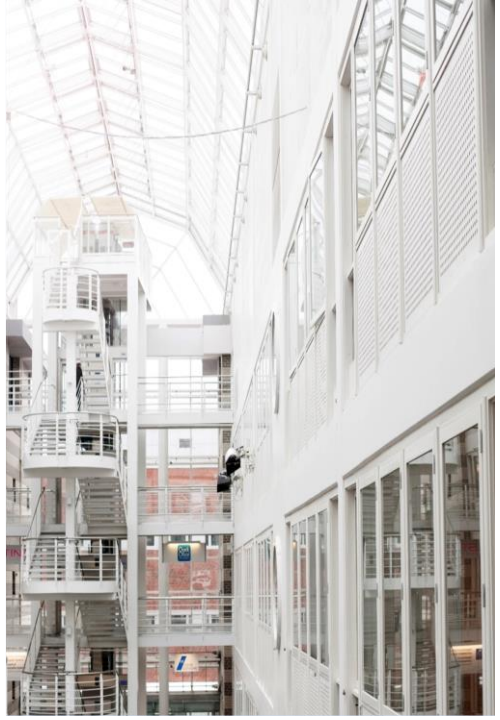


OUTLINE

1) Validation of analytical methods for H2 impurities analysis
2) Analytical methods review for performing hydrogen purity testing




1) Validation of analytical methods for H2 impurities analysis



H2 specifications according to ISO 14687 and EN 17124 standards

Component	ISO 14687 -2 µmol/mol	ISO 14687 (new) EN 17124 µmol/mol
Helium	300	300
Nitrogen	100	300
Argon	100	300
Methane	/	100
Oxygen	5	5
Carbon dioxide	2	2
Carbon monoxide	0.2	0.2
Water	5	5
Total Hydrocarbons (non methane)	2	2
Total Sulfured compounds	0.004	0.004
Ammonia	0.1	0.1
Formaldehyde	0.01	0.2
Formic acid	0.2	0.2
halogenated compounds	0.05	0.05

Standards to take into account:

- ISO 14687-2:2012: Hydrogen fuel – product specification – Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles –
- ISO FDIS 14687- Hydrogen fuel quality — Product specification (revision of previous one) to be published in 2019
- EN 17124 - 2018: Hydrogen fuel — Product specification and quality assurance — Proton exchange membrane (PEM) fuel cell applications for road vehicles

Analytical Challenges

- Many compounds to analyze (14 impurities)
- Large range of concentrations : from 0.004 to 300 µmol/mol
- Low and therefore challenging thresholds for some species (S- compounds and halogenated ones)
- Total species: cover a large number of species!

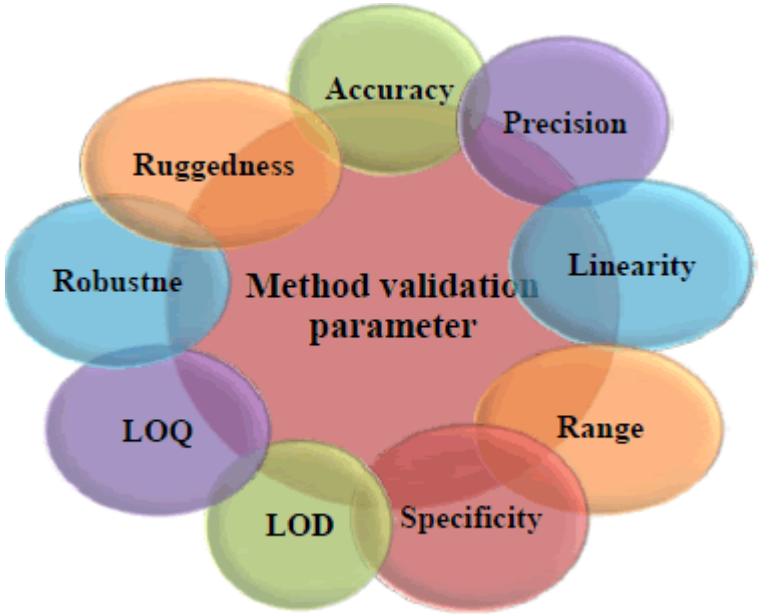
Component	ISO 14687 -2 µmol/mol	ISO 14687 (new) EN 17124 µmol/mol
Helium	300	300
Nitrogen	100	300
Argon	100	300
Methane	/	100
Oxygen	5	5
Carbon dioxide	2	2
Carbon monoxide	0.2	0.2
Water	5	5
Total Hydrocarbons (non methane)	2	2
Total Sulfured compounds	0.004	0.004
Ammonia	0.1	0.1
Formaldehyde	0.01	0.2
Formic acid	0.2	0.2
halogenated compounds	0.05	0.05

Validation of analytical methods for hydrogen impurity analysis ISO 21087

- **Title**
  - *Gas analysis — Analytical methods for hydrogen fuel — Proton exchange membrane (PEM) fuel cell applications for road vehicles*
- **Scope**
  - This document specifies the **validation protocol** of analytical methods used for ensuring the quality of the gaseous hydrogen quality at hydrogen distribution bases and hydrogen fueling stations for proton exchange membrane (PEM) fuel cells for road vehicles.

Validation of analytical methods for hydrogen impurity analysis ISO 21087

- *Method validation* is the process used to confirm that the analytical procedure employed for a specific test is suitable for its intended use.
- Analytical methods need to be validated before their introduction into routine use
- There are a number of parameters to assess for validation.



Validation of analytical methods for hydrogen impurity analysis ISO 21087

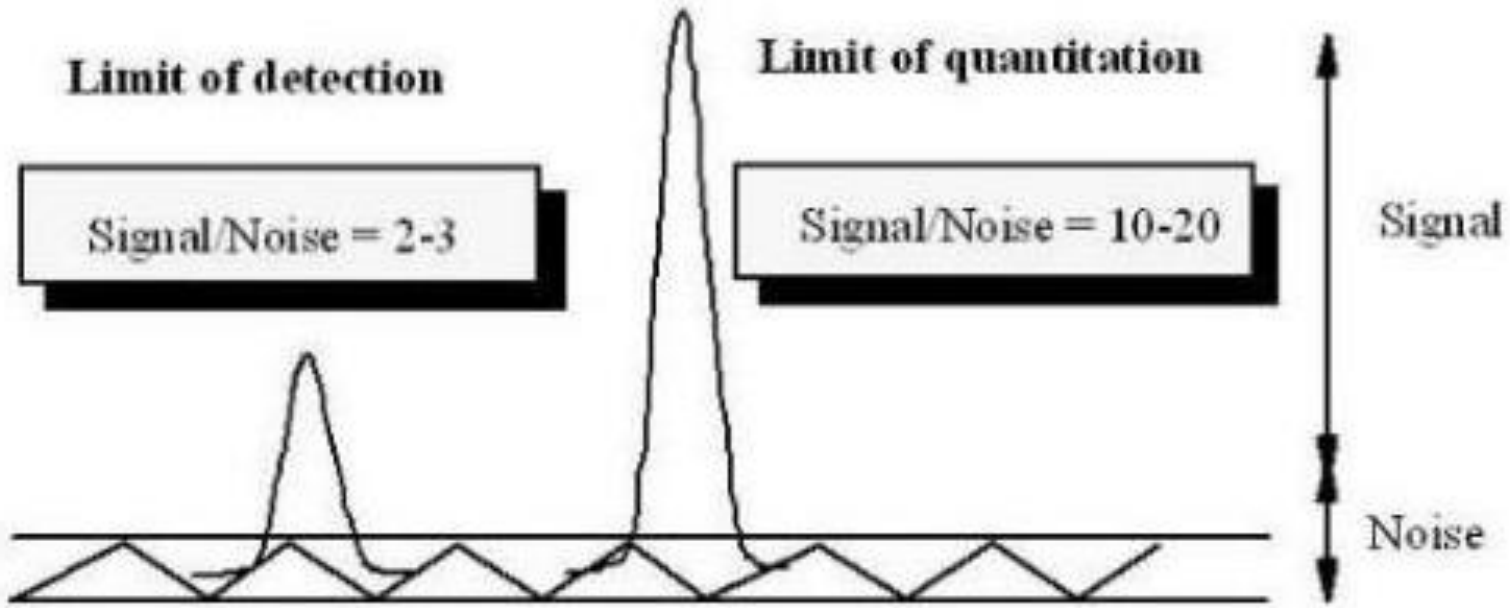
Performance characteristic	Type of analytical application			
	Identification test	Quantitative test for impurity	Limit test for impurity	Quantification of main component
Selectivity	x	x	x	x
Limit of detection			x	
Limit of quantification		x		
Working range including linearity		x		x
Trueness (bias)		x		x
Precision (repeatability and intermediate precision)		x		x
NOTE The table is simplified and has been adapted to the structure and terminology used in this Guide.				

Source : Eurochem guide on fit for purpose of analytical method

Selectivity

- Definition
  - Analytical selectivity relates to “the extent to which the method can be used to determine particular analyte in mixtures or matrices without interferences from other components of similar behaviour
- Procedure
  - Literature review: Main compounds effect (ex.: H2O, N2, O2, CO2, He, CH4)
  - Test with real samples containing interferences identified or standards with interferences identified
- Calibration using non hydrogen matrix gas
  - Equivalence with hydrogen matrix must be proven

Limit of Detection / Limit of quantification



Suitable samples for estimating standard deviation s'_0 near detection limit:

1) Blank samples, i.e. matrices containing no detectable analyte (noise)
2) Test samples with concentrations of analyte close to or below the expected LOD (signal)

Limit of Detection / Limit of quantification

- Definition
  - Limit of detection

$$LOD = 3 \times s'_0$$

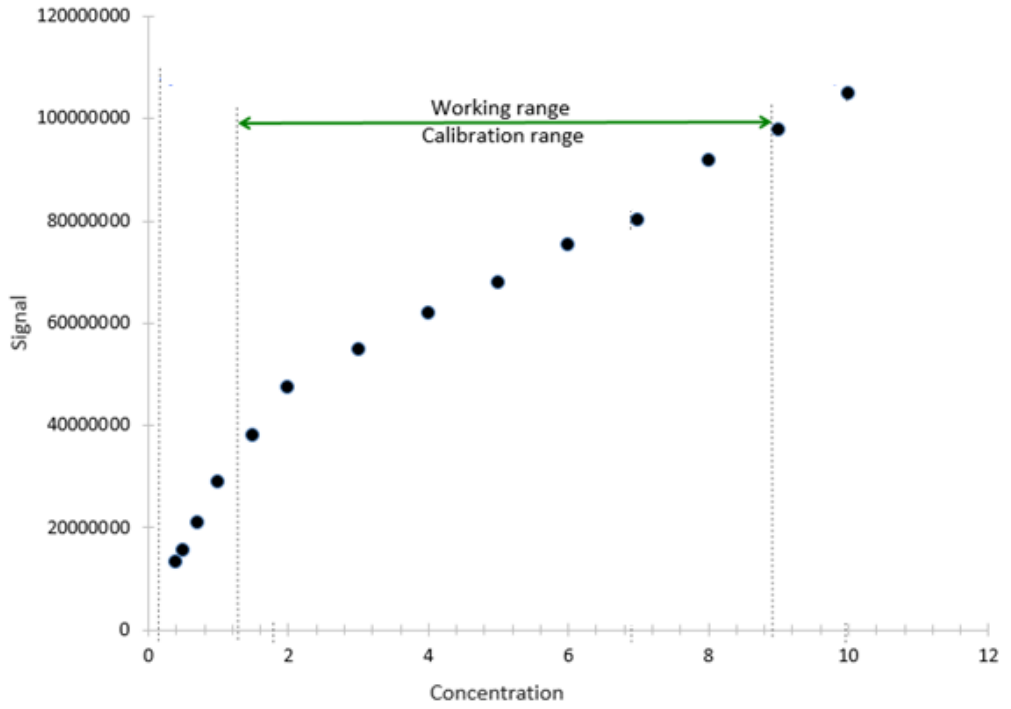
  - Limit of quantification:
    - Calculate LOQ = k_q x s'_o
    - k_q is usually 10 but other values such as 5 are commonly used
    - for threshold value < 1 µmol/mol and > 10 nmol/mol
      - LOQ = 5 x S_0
- Criteria for ISO 21087:

$$LOQ + u_{\mathrm{LOQ}} < \text{threshold value}$$

Compounds	LOD needed
CO	Yes
Halogenated	Yes
Formic acid	Yes
Formaldehyde	Yes
Ammonia	Yes
Total sulphur	Yes
H_2O	Depends on the technique
Total hydrocarbons	Depends on the technique
CO_2	No
CH_4, N_2, Ar, He	No

Working range

- Definition
  - The lower end of the working range is generally bounded by the LOQ.
  - The upper end of the working range is defined by the concentration at which significant anomalis in the analytical sensitivity are observed (end of model linearity or saturation of the signal)
- Criteria for 21087:
  - the higher value of the working range shall be at least equal to 2 times the threshold value

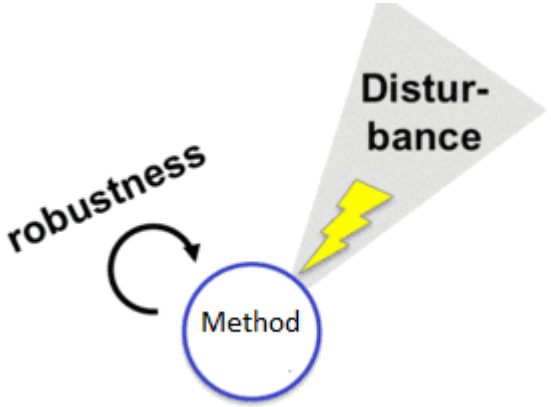


Robustness

Robustness

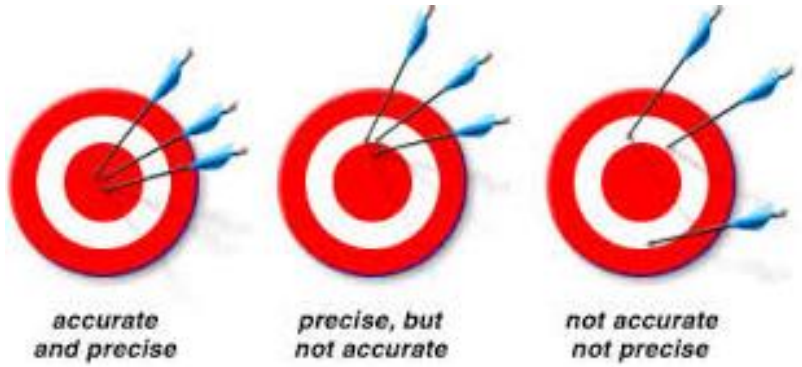
The **robustness**/ruggedness of an analytical procedure is a measure of its capacity to remain unaffected by small, but deliberate variations in **method** parameters and provides an indication of its reliability during normal usage

Ruggedness



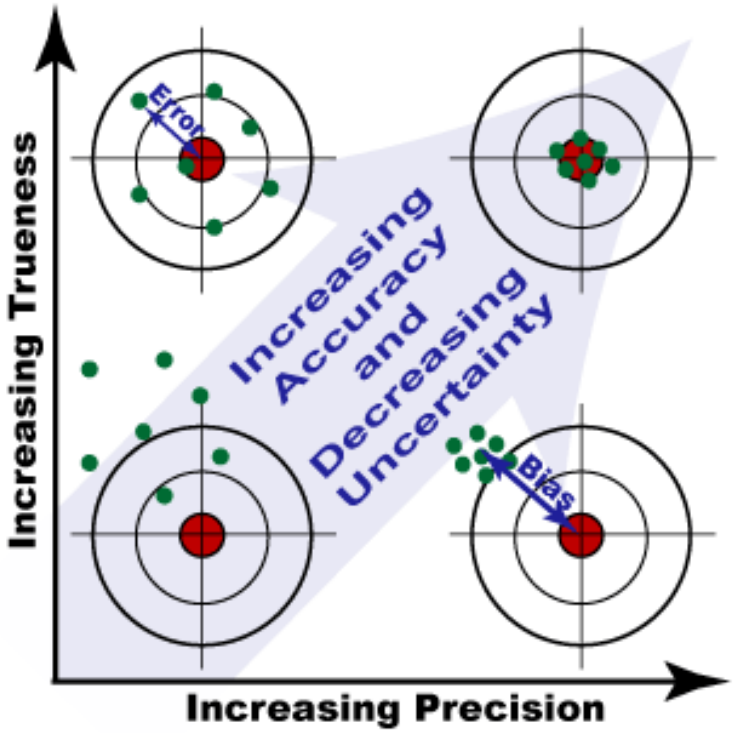
Trueness

- Definition
  - Determination of the trueness is based on the measurement of bias and relies on comparison of the mean of the results (xmean) obtained from the method with a suitable reference value (xref)
- Criteria for 21087:
  - the bias of the method shall be determined at concentrations close to the threshold value
  - This bias shall be small enough to have a relative standard uncertainty below 10 % of the concentration (except for sulfured compounds)



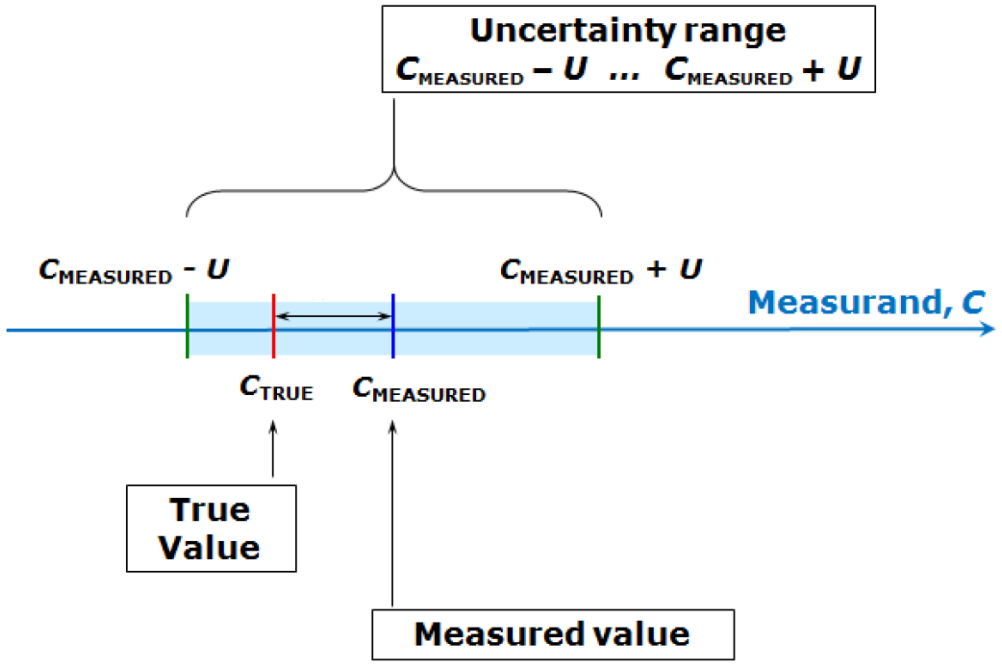
Precision

- Definition
  - Measurement precision is a measure of how close results are to one another. It is usually expressed by the standard deviation calculated from results obtained by carrying out replicate measurements
- Criteria for 21087:
  - Precision of the method shall be determined at least at concentrations close to the threshold value
  - Precision for this concentration shall be small enough to have a relative standard measurement uncertainty below 10 % of the concentration (except for sulfured compounds)



Uncertainty

- Definition
  - The uncertainty is mainly due to trueness (bias) and precision plus the impact of calibration or external parameters like temperature or pressure.
- Criteria for 21087:
  - The concentration, close to the threshold value, should be measured using the developed analytical method. The relative combined uncertainty for that concentration should be below 10 % relative (except for sulfured compounds)



Uncertainty

Combined uncertainties (precision, bias..)

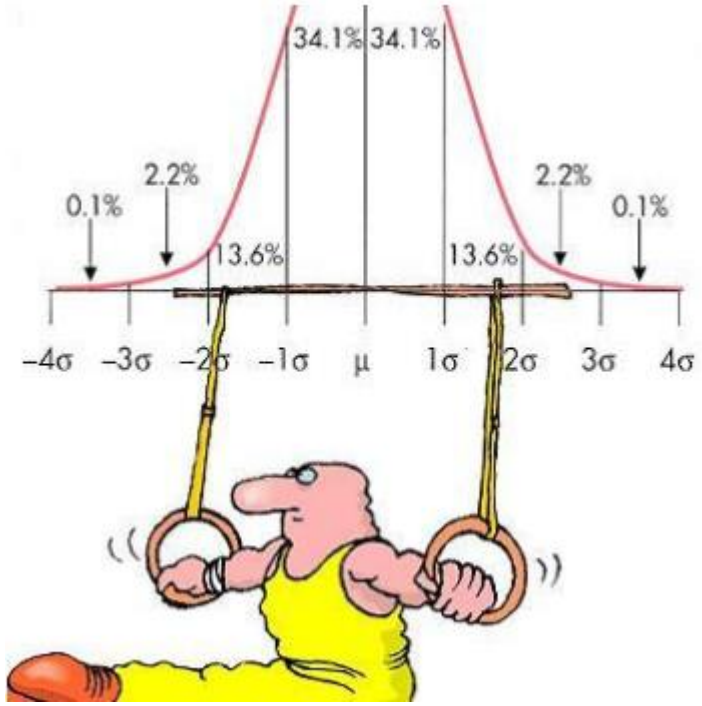
$$CU = \sqrt{u_1^2 + u_2^2 + \cdots + u_n^2}$$

Expanded uncertainty:

$$EU = k \cdot CU$$

k: coverage factor

k = 2: 95% confidence interval means that 95 measurement results out of 100 will statistically be within the limits of the uncertainty estimates.



Validation of analytical methods for hydrogen impurity analysis ISO 21087

Global protocol

	What to do?	How?		
Selectivity	Check for possible Interferences	Literature review	Study the method´s ability to measure the analyte in samples to which specific interferences have been deliberately introduced	Study the method´s ability to measure the analyte compared to other independent methods (if it is unclear whether or not interferences are already present)
	Check eventual matrix effects	Literature review	Comparison of calibration using non hydrogen matrix gas and hydrogen matrix gas	
LOD	Replicated measurements of blank samples or samples with low concentrations of analyte (m = 10)	Calculate the standard deviation s_o of the results expressed in concentration units	Calculate s'_o*: (a) $s'_o = \frac{s_o}{\sqrt{n}}$ or (b) $s'_o = \sqrt{\frac{1}{n} + \frac{1}{n_b}}$ if blank is substracted	Calculate LOD = 3 x s'_o
LOQ	Calculation from LOD	Calculate the standard deviation s_o of the results expressed in concentration units	Calculate s'_o*: (a) $s'_o = \frac{s_o}{\sqrt{n}}$ or (b) $s'_o = \sqrt{\frac{1}{n} + \frac{1}{n_b}}$	Calculate LOQ = k_q x s'_o k_q is usually 10 but other values such as 5 or 6 are commonly used
Working range	1) Measure blank + calibration standards at 6-10 concentrations evenly spaced across the range of interest	Plot response against concentration	Visually examine to identify approximate linear range and upper and lower boundaries of the working range for the instrument	
	2) Measure blank + calibration standards 2-3 times at 6-10 concentrations evenly spaced across the linear range	Calculate appropriate regression statistics		

Validation of analytical methods for hydrogen impurity analysis ISO 21087

Global protocol

	What to do?	How?		
Trueness	Select a Reference Material (RM) – m = 10 at a concentration preferably close to ISO14687 threshold	Calculate the bias b (abs. and rel.)	$b_{abs} = \bar{x} - xr_{ef}$ $b_{rel} \frac{\bar{x} - xref}{xr_{ef}} \times 100$	If sample preparation is a part of the method, calculate recovery $R(\%) = \frac{\bar{x}}{xr_{ef}} \times 100$
Precision	Intermediate precision: Measure RMs, samples or spiked blanks at various concentration across working range on different days / different operators – 6 to 15 replicates per measurement occasions	Perform statistical study to determine repeatability effects from day-to-day / operator-to-operator. Calculate standard deviation (s) of results	ANOVA statistical tool can be used	
Ruggedness	Identify variables which could have a significant effect on method performance Ex: pressure, flow rate…	Determine the effect of each change of condition on the measurement results	Eventually, state suitable tolerance limits for these variables	

Validation of analytical methods for hydrogen impurity analysis ISO 21087

validation report

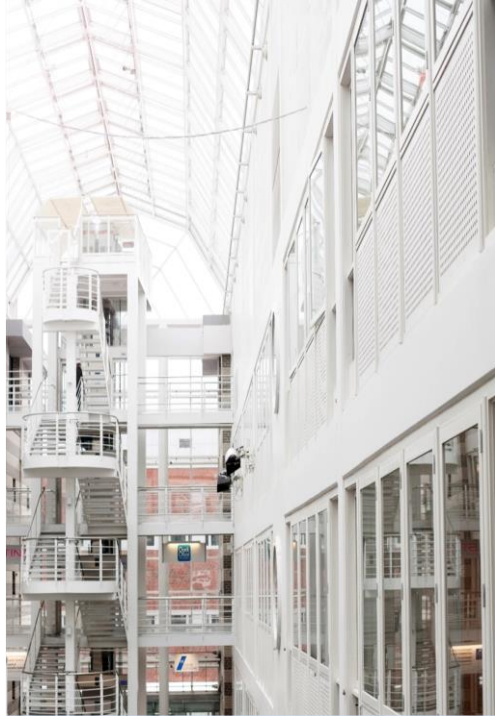
- Definition
  - A validation report describing all the tests done for the evaluation of all the characteristics of the analytical methods should be done. This report should be presented upon request.
- Criteria for 21087:
  - Each laboratory shall verify the performance of the method against the fitness for purpose acceptance criteria of this document before introducing them
  - If the method doesn’t fulfil these criteria, it shall not cannot be used for the analysis of impurities in H2; another method shall be used

Validation of analytical methods for hydrogen impurity analysis ISO 21087

practical example

- Analysis of N2 with GC/TCD:
  - To complete if possible

2) Analytical methods review for performing hydrogen purity testing



Analytical methods review for performing hydrogen purity testing according to ISO 14687-2 standard – Approach

- Literature review of currently available impurity analysis methods
  Source: ASTM standards, JIS standards, in-house methods
- Discussion with instruments providers – innovative methods?
- Discussion with instruments users - Feedbacks on implemented methods

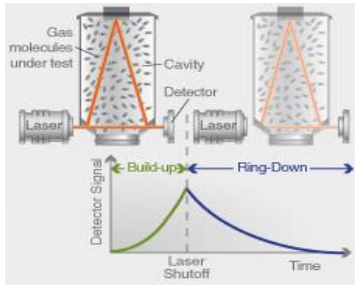
- Evaluation of the status of the methods listed in term of validation – what is done / needs to be done
- Own methods development – For total species
- Propositions for next steps – what to do now?

Multi-component analysers (other than GC-methods)

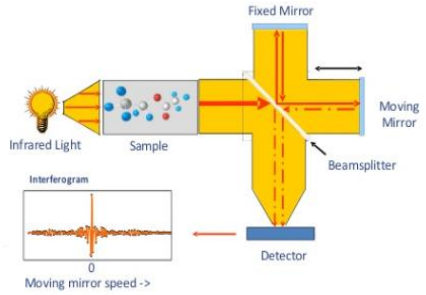
- Some instrument manufacturers now offer the possibility to use multi-component analyzers in order to reduce the number of analyses totally required – instruments need to be designed based on the **clients´specifications**

- Clients (for ex. labs) may base the specifications on different factors: taking into consideration other instruments already available at the laboratory or focusing on impurities based on probability of presence or/and impact of impurities of fuel cell system.

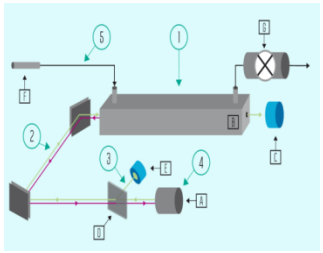
- The clients will need to decide on requirements for characteristic performances, costs and possibly other specific requirements (response time, volume the gas needed, possibility to work with different gas matrices)



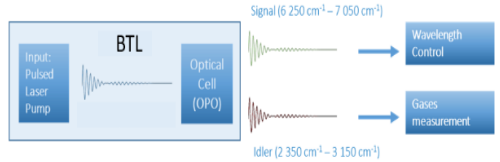
CRDS



FTIR



OFCEAS



BTL

Analytical procedures and multi-components analyser

Performance assessment of multi-component analysers

- Not turnkey solutions commercially available
- Need to be designed based on the clients' specifications
- Specifications and performances need to be assessed as sensitivity, selectivity, reproducibility

Methods are being compared in terms of:

- ✓ **Nature and number of analysed compounds**
- ✓ **Limit of Detection**
- ✓ **Uncertainty measurement**
- ✓ **Number of instruments required**
- ✓ **Connection**
- ✓ **Volume/flow and pressure of gas needed**
- ✓ **Costs**

Method under study

OFCEAS

FTIR

BTL

CRDS

Hydrogen

RI. SE

Assessment of the performances of instruments enabling the simultaneous analysis of compounds mentioned in ISO 14687-2

	CRDS	FTIR	OFCEAS	BTL
Water	Instrument 1	Instrument 1	Instrument 1	
Oxygen	Instrument 4		Instrument 2	Need dev.
Carbon dioxide	Instrument 1	Instrument 1	Instrument 2	
Carbon monoxide	Instrument 1	Instrument 1	Instrument 1	Need dev.
Formaldehyde	Instrument 3	Instrument 1	Instrument 1	
Formic acid		Instrument 1	Instrument 1	
Ammonia	Instrument 2	Instrument 1	Instrument 1	Need dev.
Helium				
Total nitrogen and argon				
Total hydrocarbons		Methane, ethane…		
Methane	Instrument 1	Instrument 1	Instrument 1	yes
Total sulfur compounds				
Hydrogen sulfide			Instrument 1	Need dev.
Total halogenated compounds				
Hydrogen chloride	Instrument 5		Instrument 2	Yes
Hydrogen bromide				yes
Number of instruments required	4 (5 with HCl)		2 racks 19inch 4U and external ump	All in one instrument
Combined price	170 -185 k€	80 – 100 k€	160 -180 k €	70-90 k€
Instruments connection	In parallel		Total sample consumption 20 l/h at atmospheric pressure Connection Swagelock ¼inch Analysers should be in series	Digital signal RS 232 Gas ports Swagelock 1/8
Contact	Tiger Optics, Florian Adler	MKS and a Swedish distributor (ROWACO)	AP2E Etienne Smith	Blue Industry and Science, Olivier Le Mauguen
Volume/flow and pressure of gas needed	12 l/h	30-60 l/h	20 l/h	< 100 ml total, Low pressure

List of instrument specifications for the development of multi-component analysers using input from A1.3.1

In table 5, the criteria and requirements discussed in the section above are summarized.

	Criteria	Requirements / Action / evidences
Simultaneous analysis of several compounds	List of compounds analysed	compare to priority lists
Specifications related to method performances		
Detection limit/quantification limit	LOQ + uLOQ (k=2) < ISO 14687	Verify detection limit with analysis of PRM
Working range	Preferably 10 * ISO 14687 (at least 2* ISO 14687)	Provide linearity plot
Selectivity (normal)	Interferences versus ISO 14687 composition	Literature or experiments If possible use PRM cocktail at ISO 14687 level
Selectivity (extrem)	Interference versus critical situation observed in real situation	Literature / Technical evidences
Precision	< 10 % rel at ISO level	use of PRM at ISO threshold
Trueness	< 10 % rel at ISO level	use of PRM at ISO threshold
Measurement uncertainties	< 20 % rel at ISO level < 50% CH2O and Sulphur	Provide calculation and equation including at least uC = $\sqrt{u(Rw)2+u(bias)2}$

List of instrument specifications for the development of multi-component analysers using input from A1.3.1

Other important criteria are:

- Costs: Not only equipment costs but also maintenance and operation costs
- Volume of gas needed (incl. flow rate)
- Analysis time (incl. stabilisation time)

Review of current analytical methods – living document

Sources

- ASTM standards
- JIS standards
- NMI methods: NPL, (RISE)
- Some contacts with instruments providers

Analytical technique	Impurity											
	H_2O	C_nH_m	O_2	He	N_2 / Ar	CO_2	CO	R-S	HCHO	HCOOH	NH_3	THC
	Water	Total hydrocarbons	Oxygen	Helium	Nitrogen and Argon	Carbon dioxide	Carbon monoxide	Total sulphur	Formaldehyde	Formic acid	Ammonia	Total halogenated compounds
Dew point analyzer												
Vibrating quartz crystal analyzer												
CRDS		CH4										HCl, HBr
GC-MS												
GC-MS with jet pulse injection												
FTIR		CH4, C2H6,..										
OFCEAS		CH4						H2S				
FID												
GC-FID												
Methane GC-FID												
ECD												
GC-TCD												
GC-PDHID												
GC-SCD with concentrator												
GC-SCD without pre-concentration												
DNPH-HPLC-UV												
IC with concentrator												
IC-CD												
HPLC-CD												
CIC												
GC-ELCD												
TD-GC-MS								organic				
Galvanic cell O2 meter												
ICP-MS												No F cpds

Current status in term of validation

Table 2: Identified performance characteristics among LOQ (Limit of Quantification), selectivity, working range, precision, trueness and ruggedness that requires further evaluation

Methods	Compounds	LOD	Selectivity	Working range	Precision	Trueness	Ruggedness	Standardised methods	Methods information in public domain	In-house methods
OFCEAS	H2O									Under evaluation by RISE
	O2									
	CO									
	CO2									
	CH2O									
	CH2O2									
	NH3									
	H2S									To be validated, RISE (16ENG01)
	CH4									
	HCl									
	HBr									
CRDS	H2O							ASTM D7941-14		NPL in house methods
	O2							ASTM D7941-14		
	CO2							ASTM D7941-14		
	CO							ASTM D7941-14		
	CO									VSL in house methods
	CH2O2									VSL in house methods
	NH3							ASTM D7941-14		VSL in house methods
	CH4							ASTM D7941-14		VSL in house methods
	HCl									VSL in house methods
	HBr									

Green: validated
Yellow: some information available
Orange: need to be validated

Hydrogen RISE

Current status in term of validation

Table 2: Identified performance characteristics among LOQ (Limit of Quantification), selectivity, working range, precision, trueness and ruggedness that requires further evaluation

Methods	Compounds	LOD	Selectivity	Working range	Precision	Trueness	Ruggedness	Standardised methods	Methods information in public domain	In-house methods
FTIR	H2O							ASTM D7653-10		
	CO2							ASTM D7653-10		
	CO							ASTM D7653-10		
	CH2O							ASTM D7653-10		VSL in house methods
	CH2O2							ASTM D7653-10		NPL in house methods
	NH3							ASTM D7653-10		NPL in house methods
	CH4							ASTM D7653-10		
GC-TCD	O2									NPL in house methods
	He									NPL in house methods
	N2									NPL in house methods
	Ar									
GC-FID	CH4									Validated by RISE, activity A2.2.3 [2]

Current status in term of validation

Table 2: Identified performance characteristics among LOQ (Limit of Quantification), selectivity, working range, precision, trueness and ruggedness that requires further evaluation

Methods	Compounds	LOD	Selectivity	Working range	Precision	Trueness	Ruggedness	Standardised methods	Methods information in public domain	In-house methods
GC-MS	H2O							ASTM D7649-10		
	O2							ASTM D7649-10		
	He							JIS K 0123		
	N2							ASTM D7649-10		
	CO2							ASTM D7649-10		
	Ar							ASTM D7649-10		
	NH3									
	CH2O							ASTM D7892-15		
	Hydrocarbons							ASTM D7892-15		
	Organic sulfur									
	Organic halides							ASTM D7892-15		To be validated (16ENG01)
Dew point hygrometer	H2O							JIS K0225		NPL in house methods
Vibrating quartz crystal analyzer	H2O							JIS K0225		NPL in house methods
Electrochemical sensor	O2							ASTM D7607-11		
GC-PDHID	O2								Rapport NPL [3]	NPL in house methods
	N2									NPL in house methods
	Ar									NPL in house methods
	CO2									
Galvanic cell O2 meter	O2							JIS K0225		
Methanizer GC-FID	CO									VSL and NPL in house

Method developments – for total species

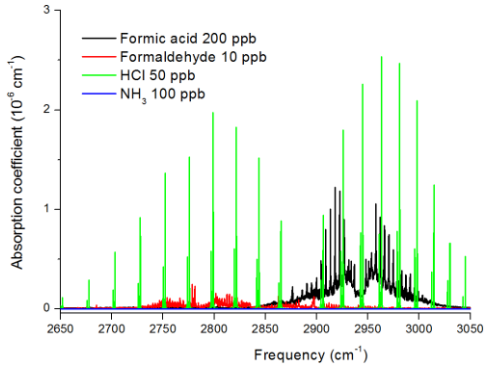
Determination of total species is a real analytical challenge:

- They cover a large number of species
- Quantification mostly based on conversion of compounds into one species (problem with interferences or compounds not efficiently converted)

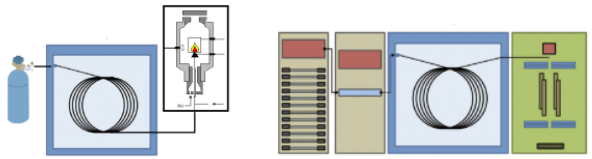
Only a few impurities of a total species group may actually be present in the hydrogen:

- Developing a speciation method allow to measure the actual impurities
- Possibility to suggest to ISO/TC 197 to replace ”total species” with the actual impurities

A2.2.1: cryo-GC-SCD for sulfur species



A2.2.2: CRDS for HCl



A2.2.3: GC-FID + TD-GC-FID/MS for hydrocarbons species

Current status in term of validation

Conclusions:

- Many methods exist for all the species to analyze in ISO14687-2
- Multi-components analyzers promising but instruments need to be designed based on the **clients´specifications** (and it will be several instruments most of the time)
- Evidently, there is a need to further validate the methods proposed
- Total species: often very challenging

Available documents for more information

- Report ”Literature review of impurity analysis methods for the compounds mentioned in ISO 14687-2:2012” (A2.1.1)
- Report ”Plan for the further development of analytical methods taking into account their performance chracteristics” (A2.1.3)
- Report ”Instrument specifications for the development of multi-component analysers using input from A1.3.1” (A2.2.4)
- Report ”Assessment report of a multi-component analyser with optimised sampling analysis that meets the required detection limits as per business plans ISO/TC197 and CEN/TC268” (A2.2.6)

Available on the website of the project: https://projects.lne.eu/jrp-hydrogen/

Practical example: Method validation for methane with GC/FID

Method: Methane is analysed by GC/FID (gas chromatography with flame ionization detector) using helium as a carrier gas and a Porous Layer Open Tubular (PLOT) column which is well suited for the analysis of light hydrocarbons.

Validation parameters to be evaluated:

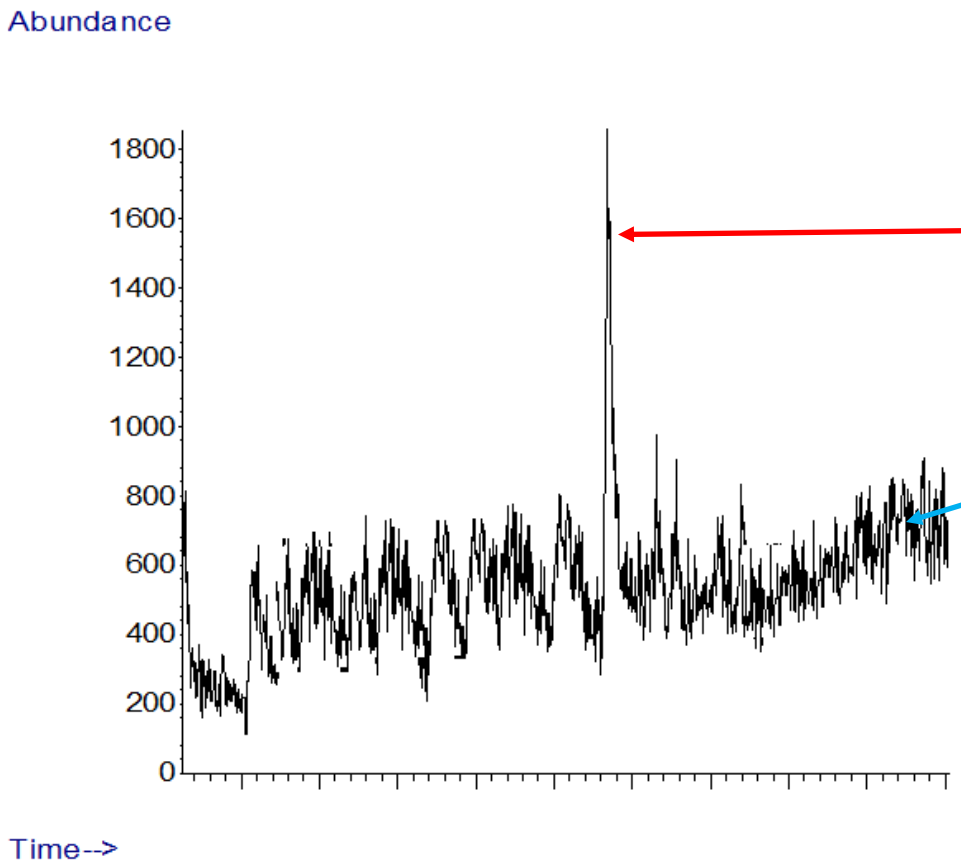
- LOD – by signal/noise method at levels close to the LOD
- LOQ - by signal/noise method at levels close to the LOD
- Precision – within-laboratory reproducibility (Rw) - Measure RMs, samples or spiked blanks at various concentration across working range on different days / different operators – 6 to 15 replicates
- Trueness – bias determination using Reference material - select a Reference Material (RM) – m = 10 at a concentration preferably close to ISO14687 threshold

Practical example: Calculation of LOD and LOQ

ISO 21087: suitable samples for estimating LOD and LOQ:

1) Blank samples, i.e. matrices containing no detectable analyte
2) Test samples with concentrations of analyte close to or below the expected LOD

Methane at 0.5 µmol/mol in hydrogen analysed by GC/FID:



Signal	Noise
1800 – 400 = 1400	600 – 200 = 400

S/N = 1400/400 = 3.5

LOD (S/N=3)	LOQ (S/N=10)
0.5 µmol/mol · 3/3.5 ≈ 0.4 µmol/mol	0.5 µmol/mol · 10/3.5 ≈ 1.4 µmol/mol

Practical example: Calculation of the uncertainty

In this case, we consider that the two main sources of uncertainties are the one for the within laboratory Reproductibility (Rw) and the one for the trueness (bias). Other sources are negligible.

If $u(R_w)$ = 3.4% and u(bias) = 1.6%, calculate CU and EU (rel.)

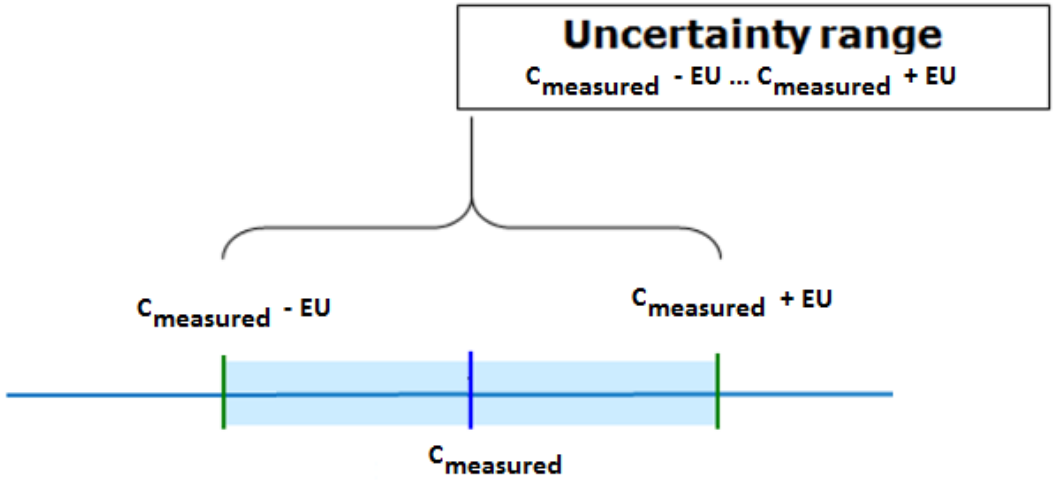
CU	EU (k=2)
$=\sqrt{3.4^2 + 1.6^2} \approx 4$ %	= 2 · 4% = 8%

1.5 µmol/mol · 8% = 0.12 µmol/mol

If analysis result: Methane 1.5 µmol/mol, calculate the uncertainty range:

Uncertainty range
(1.5 ± 0.12) µmol/mol

1.38 … 1.62 µmol/mol



Combined uncertainties (precision, bias..)

$$CU = \sqrt{u_1^2 + u_2^2 + \cdots + u_n^2}$$

Expanded uncertainty:

$$EU = k \cdot CU$$

INTERNATIONAL WORKSHOP

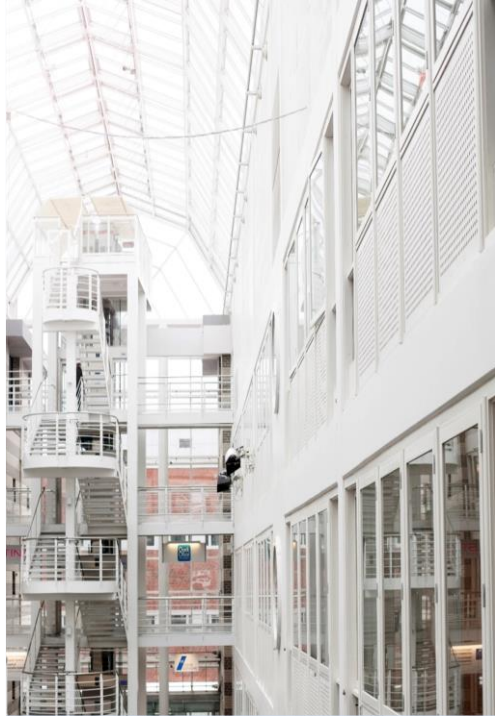
METROLOGY FOR SUSTAINABLE HYDROGEN ENERGY APPLICATIONS

7 –8 NOVEMBER 2018

Oliver Büker

Martine Carré

Thank you!



Analytical methods review for performing hydrogen purity testing according to ISO 14687-2 standard – Methods shall be fit-for-purpose

ISO 21087: precision