Metrology for sustainable hydrogen energy applications

JRP EMPIR 15NRM03
HYDROGEN

WP2: Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO 14687-2 standard

Task 2.2: Methods development

A2.1.3: Plan for the further development of analytical methods taking into account their performance characteristics

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Summary

As there is a relatively large panel of analytical methods that can be implemented for each parameter to be analysed in the ISO standard 14687-2, the analyst may need to take a decision on which instrument to select or buy.

An important criterion to guide the choice of the analyst is the performance characteristics of the method that will be implemented on the analytical instrument. However, this information is not always easily available and the main focus of instrument providers has so far been on the quantification limits as these are clearly challenging to reach.

In this report, we have summarized the information collected in the activity A2.1.2 (comparison of methods with regard to performance characteristic) in order to discuss for each method which are the performance characteristics that require further evaluation. The results are presented in a table together with a discussion.

Once the choice has been made, the analyst will need to verify if the method works in the end-user´s laboratory (fit-for-purpose).
 In this report, we refer to relevant documents in order to assist in the validation process. A summary of the steps needed in the validation process is presented in a table.

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1   Introduction

As it has been shown in the previous activities of the task "Methods development", there is a relatively large panel of analytical methods that can be implemented for each parameter to be analysed in the ISO standard 14687-2 [1]. The standard provides a list of suggested analytical methods but rightfully indicates that the technologies and equipment are in continual development towards better performances.

In the activity A2.1.2 of this project, available methods were compared with regards to performance characteristics. Most of the information available for each method focused on the quantification limits as these are clearly challenging to reach. Other performance characteristics i.e. repeatability, accuracy are not always disclosed (in standards or by instrument providers) or are expressed in ways that do not allow a direct comparison of the methods. Moreover, the methodologies followed to measure the reported performance characteristics are not clearly specified.

In this report, we have summarized the information collected in the activity A2.1.2 in order to discuss for each method which are the performance characteristics that require further evaluation. The results are presented in a table together with a discussion in a text form.

In the second part of this report, we summarized the process to follow in order to validate the methods.

This information would be useful/beneficial to laboratories that would like to implement ISO 14687-2 and therefore may need to purchase or select some equipment/instrument.

The latest developed multi-component instruments have the potential to meet the required detection limits according to ISO14687-2. However, these instruments need to be designed based on the client´s specifications (number of compounds to be analysed simultaneously, the analytical measuring range…). These will also benefit of such a plan. Once the instrument is sent to the customer, it is recommended that the validation data received from the instrument´s manufacturers are also evaluated by the end-user.

2   Suggested analytical methods

The following methods have been identified in A2.1.2 as methods that can be implemented to determine one or several of the impurities/families of impurities from ISO14687-2:

Table 1: Methods identified in A2.1.2

Acronym	Full name
CRDS	cavity ring-down spectroscopy
GC-MS	gas chromatography - mass spectrometry
FTIR	Fourier transform infrared spectroscopy
OCFEAS	optical feedback cavity-enhanced absorption spectroscopy
Methanizer-GC-FID	gas chromatography -Flame ionization detector with methanizer
GC-TCD	gas chromatography – thermal conductivity detector
GC-PDHID	gas chromatography - pulsed discharged helium ionization detector
GC-SCD	Gas chromatography – sulfur chemiluminescence detector
HPLC-UV(-VIS)	High performance liquid chromatography with UV(-VIS) detection
IEC	Ion Exclusion chromatography
TD-GC-MS	Thermal desorption-gas chromatography - mass spectrometry

-	Galvanic cell O2 meter
-	Vibrating quartz crystal analyzer
-	Dew point hygrometry

3 Identified needs for further evaluation of performance characteristics of the methods

Based on the information collected in A2.1.2, the performance characteristics among LOQ (Limit of Quantification), selectivity, working range, precision, trueness and ruggedness that requires further evaluation are listed in table 2.

LOD

Most of the information available for each method focused on the quantification limits as these are clearly challenging to reach in ISO14687-2. For most of the methods developed, there is a given value for the limit of quantification that has either been evaluated by the lab having implemented the method or by the instrument´s provider.

Selectivity

Most of the methods have known criteria to evaluate the selectivity which are related to the principle of the method.
The selectivity of analytical techniques relying on monitoring targeted compounds absorption in the infrared is based on working in regions where no significant interference arises from other infrared absorbers, or by measuring interfering gases and accounting for them in the spectral fitting routine.
In chromatography, the selectivity of a GC- system refers to its capacity to retain targeted components to a significantly greater or lower extent than other components mostly when using a non-selective detector (a selective detector responds to only certain types of components). In other words, the method shall be optimized to avoid coelution of the target compound with another component which also can be present in the sample to analyse (optimization of the temperature program of the column, the flow…). For example, in most of the GC/TCD systems, it is difficult to avoid coelution between Argon and Oxygen. For open-tubular columns, there are now quite large databases that include quantitative information on selectivity and its variation with temperature.

Working range

Most of the techniques relying on monitoring targeted compounds by absorption in the infrared require custom-built instruments. Generally the lab lists requirements including a statement of a working range. The working range is also often known for GC-methods as they are used in so many other applications.

Trueness and precision

Trueness is probably the parameter that is most commonly not evaluated according to method validation guides i.e. using an appropriate reference material.
An evaluation of the precision is sometimes provided by instrument´s manufacturers, often expressed in percent (relative) or as a factor of the LOD.

Ruggedness

Ruggedness is often expressed as high if evaluated. However, experimental data when testing different values for variables which could have a significant effect on method performance (flow rate, pressure…) would need to be reported.

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	green	yellow	green	yellow	orange	orange			Under evaluation by RISE
	O2	green	yellow	green	yellow	orange	orange			
	CO	green	yellow	green	yellow	orange	orange			
	CO2	green	yellow	green	yellow	orange	orange			
	CH2O	green	yellow	green	yellow	orange	orange			
	CH2O2	green	yellow	green	yellow	orange	orange			
	NH3	green	yellow	green	yellow	orange	orange			
	H2S	green	yellow	green	yellow	orange	orange			To be validated, RISE (16ENG01)
	CH4	green	yellow	green	yellow	orange	orange			
	HCl	green	yellow	green	yellow	orange	orange			
	HBr	green	yellow	green	yellow	orange	orange			
CRDS	H2O	green	yellow	green	orange	orange	orange	ASTM D7941-14		NPL in house methods
	O2	green	yellow	green	orange	orange	orange	ASTM D7941-14		
	CO2	green	yellow	green	orange	orange	orange	ASTM D7941-14		
	CO	green	yellow	green	orange	orange	orange	ASTM D7941-14		
	CO	green	yellow	green	orange	orange	orange			VSL in house methods
	CH2O2	green	yellow	green	orange	orange	orange			VSL in house methods
	NH3	green	yellow	green	orange	orange	orange	ASTM D7941-14		VSL in

		🟩	🟨	🟩	🟧	🟧	🟧			house methods
	CH4	🟩	🟨	🟩	🟧	🟧	🟧	ASTM D7941-14		VSL in house methods
	HCl	🟩	🟨	🟩	🟧	🟧	🟧			VSL in house methods
	HBr	🟩	🟨	🟩	🟧	🟧	🟧			
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]

Technique	Component							Method	Ref	Notes
GC-MS	H2O	green	yellow	orange	orange	orange	orange	ASTM D7649-10		
	O2	green	yellow	orange	orange	orange	orange	ASTM D7649-10		
	He	green	yellow	orange	orange	orange	orange	JIS K 0123		
	N2	green	yellow	orange	orange	orange	orange	ASTM D7649-10		
	CO2	green	yellow	orange	orange	orange	orange	ASTM D7649-10		
	Ar	green	yellow	orange	orange	orange	orange	ASTM D7649-10		
	NH3	green	yellow	orange	orange	orange	orange			
	CH2O	green	yellow	orange	orange	orange	orange	ASTM D7892-15		
	Hydrocarbons	green	yellow	orange	orange	orange	orange	ASTM D7892-15		
	Organic sulfur	green	yellow	orange	orange	orange	orange			
	Organic halides	green	yellow	orange	orange	orange	orange	ASTM D7892-15		To be validated (16ENG01)
Dew point hygrometer	H2O	green	yellow	green	orange	orange	orange	JIS K0225		NPL in house methods
Vibrating quartz crystal analyzer	H2O	green	yellow	green	orange	orange	orange	JIS K0225		NPL in house methods
Electrochemical sensor	O2	green	orange					ASTM D7607-11		
GC-PDHID	O2	green	yellow	green	orange	orange	orange		Rapport NPL [3]	NPL in house methods
	N2	green	yellow	green	orange	orange	orange			NPL in house methods
	Ar	green	yellow	green	orange	orange	orange			NPL in house methods
	CO2	green	yellow	green	orange	orange	orange			
Galvanic cell O2 meter	O2	green	yellow					JIS K0225		
Methanizer GC-FID	CO	green	yellow	green	orange	orange	orange			VSL and NPL in house

Method	Analyte								Standard / Notes
		Green	Yellow	Green	Orange	Orange	Orange		methods
	CO2	Green	Yellow	Green	Orange	Orange	Orange		NPL in house methods
	CH2O	Green	Yellow	Green	Orange	Orange	Orange		NPL in house methods
	CH4	Green	Yellow	Green	Orange	Orange	Orange		NPL in house methods
	Total volatile hydrocarbon at 65°C	Green	Yellow	Green	Orange	Orange	Orange		NPL in house methods
HPLC-UV	CH2O	Green	Yellow	Orange	Orange	Orange			
IEC	CH2O2	Green	Yellow	Orange	Orange	Orange			
UV-Vis	NH3	Green	Yellow	Green	Orange				
GC-SCD	Total sulfur	Green	Green	Green	Orange	Orange			Validated by NPL in A2.2.1 [4]
Filter with IC	NH3							ASTM D7550-09	
	CH2O2							ASTM D7550-09	
C-ECD	HCl							ASTM WK23815	
	Cl2								
	Halides								

Green: Performance characteristics already evaluated
Yellow: Performance characteristics which need further evaluation but where some information is already available
Orange: Performance characteristics needing evaluation

Based on the above table, none of the analytical methods currently available for hydrogen purity measurement can be directly used without at least validation steps in the laboratory implementing them. It is a requirement to demonstrate the fit for purpose of the analytical method before reporting results. Several points of the method validations are highlighted in this report, in ISO 21087 and Eurachem guide "The Fitness for purpose of analytical methods" [5] are useful documents to complete the method validation.

4 Considerations about validation

The validation of an analytical method allows assessing the method suitability for a particular purpose.

The validation of the method gathers experimental work done to demonstrate that the method works in the end-user´s laboratory. Several parameters are considered as performance characteristics commonly evaluated during method validation: selectivity, limit of detection (LOD) and limit of quantification (LOQ), working range, trueness (bias, recovery), precision (repeatability, intermediate precision and reproducibility) and robustness.

The evaluation of a sufficient number of these parameters is required to calculate the measurement uncertainty associated with a method for a component to be measured in a specified matrix.

Several documents are available to guide a laboratory through a method validation including the Eurachem guide "The Fitness for purpose of analytical methods" [5]. Detailed information about validation process are also given in ISO21087 [6].

The method validation will provide detailed information on the capabilities, performances and limits of the analytical methods as described in the laboratory procedure and will provide a realistic and reliable measurement uncertainty budget.

The validation work shall be performed and the results reported according to a documented procedure including title (method scope, short description of the method, reference to standards, the analyte, measurand, measurement unit, types of samples, sampling), planning (purpose e.g. full validation of new method, verification of performance of a standardized method…), performance characteristics (specific requirements, outline the experiments which will be done, results and conclusions) and summary (summarize the validation work and results, conclusion to whether the method is fit for purpose).

In order to validate a method, the analyst will first need to acquire some tools (spiked materials, blanks, standards) and will then work through the validation process. Once this has been done, the conclusion on whether the method is fit for purpose can be drawn and the measurement uncertainties for a method can be calculated.

4.1 Validation tools

4.1.1 Blanks

These are essentially hydrogen with no analyte present. These are used to prepare spiked materials and for LOD/LOQ determination. These can also be used as diluent gas when producing reference gas standards.

4.1.2 Spiked materials

These are pure hydrogen samples to which the analyte(s) of interest have been deliberately added. These can be used for example in the determination of the precision.

4.1.3 Reference gas standards

Reference gas standards are mostly used in validation method to evaluate the trueness. They are also needed to determine the LOD/LOQ, the working range and can also be used to evaluate the precision. Using references gas standards traceable to SI-system and with low uncertainties will allow to reduce the final method uncertainty.

The most widely used method for the preparation of primary standard gas mixtures involves weighing the individual components into a cylinder. The accuracy of the gas mixtures prepared by gravimetry is limited by the smallest mass of gas that can be weighed and added to the mixture with an acceptable uncertainty. Primary standards are prepared in various types of cylinders, the choice of which depends on its ability to maintain the integrity of a particular gas mixture at a particular mole fraction during long-term storage.

Statically prepared gas references:

Standard gas mixtures are prepared by weighing high-purity gaseous or liquid components into cylinders. This method requires a balance for weighing the cylinder, equipment to transfer the components to the cylinder and a diluent gas. Different methods of transfer are available: capillary method (for liquid reagent), direct transfer method, the tube expansion method and the tube flush method. ISO standard 6142: 2015 [7] specifies a gravimetric method for the preparation of calibration gas mixtures in cylinders with traceable values for the amount fraction of one or more compounds.

Dynamically prepared gas references:

For some component, as formic acid, ammonia, formaldehyde and sulfur compounds, it is not always possible to produce stable mixtures with suitable long lifetimes. In these cases, an alternative approach would be to develop dynamic reference gas mixtures usually operated by diluting a high concentration stable standard with the diluent gas. There are several types of dynamic methods as described in the range of ISO 6145 standards [8]. Standard gas mixtures are prepared by weighing vessels continuously and determining a mass loss rate in a flowing stream of gas.

4.2   Validation process

Once the analytical requirement which defines the performance characteristics has been defined, the laboratory can work on the validation process where all or some of the performance characteristics shall be assessed. In this case, the analytical requirement is quite clearly defines in the upcoming standard ISO/CD 21087:2017 [6] and is treated in the report A2.2.4 "instrument specifications for the development of mutli-component analysers using input from A1.3.1".

In the table 3, the process (what to do and how) for each performance characteristics is summarized. The information presented in the table are taken from Eurachem guide "The Fitness for purpose of analytical methods" [2] and do not apply to all analytical methods but give general guidelines. In the Eurachem guide, each performance characteristic is described in detail and then a summary is presented in so called Quick References tables. A description of the performance characteristics is also given in ISO/CD 21087:2017 [6].

Table 3: Validation process

	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 $s´_o{}^*$: (b) $s´_o = \frac{s_o}{\sqrt{n}}$ 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		
Trueness	Select a Reference Material	Calculate the bias b	$b_{abs} = \bar{x}$ - xr_{ef}	If sample preparation is a part of the method,

	(RM) – m = 10 at a concentration preferably close to ISO14687 threshold	(abs. and rel.)	$b_{rel} \dfrac{\bar{x} - \text{xref}}{\text{xref}}$ x 100	calculate recovery $R(\%) = \dfrac{\bar{x}}{\text{xref}}$ x 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	

*equation depends on blank correction, if no blank correction, eq. (b), if blank correction, eq (a): n is the number of replicate observations averaged when reporting results where each replicate is obtained following the entire measurement procedure, nb is the number of blank observations averaged when calculating the blank correction according to the measurement procedure

**The highest value shall be at least equal to 2 time the limits proposed in ISO14687-2

4.3 Detection limit for one compound from a family

For hydrocarbons, sulphur and halogenated compounds, the ISO standard 14687-2 gives a limit to not exceed for the sum of the compounds of these families. It is specified that the total sulphur include at least H2S, COS, CS2 and methyl mercaptan while total halogenated compounds include hydrogen bromide, hydrogen chloride and organic halides. Total hydrocarbons include oxygenated organic species.

Dealing with families of compounds is always a challenge as many methods are speciation methods i.e. based on the principle that every compound is detected individually before all contributions are summed-up to a Total concentration. One question that arises is for example what the desired limit is for each of contribution.

Very few documents treat this problematic. However, this is somehow a bit similar to the problem of missing data. In this case, it is common to use the method of the replacement where every value below LOQ is replaced by a constant such as LOQ/2 (or LOQ/$\sqrt{2}$) [9].

5 Multi-component analyzers

As ISO 14687-2 requires the analysis of 13 gaseous species including 3 families of species, multi-component analyzers are a viable solution to reduce the number of analyses totally required. Previous activities of this project have shown that at least 3 different providers claim that they can manufacture multi-component analyzers capable of analyzing 6 to 7 impurities.

In the past, gas analyzers have often suffered interference from other components which can worsen their performances. However, multi-component analyzers can nowadays more easily measure those interferences and continuously correct the measured variable.

Tests of such instruments can include the determination of the instrument characteristic with reference gas mixtures and for example some of the following steps:

1) Check all instrument functions including collecting data for several impurities
2) Check the system´s cross sensitivity
3) Check the stability of the instrument characteristic (zero, drift)
4) Check the response time

6 Considerations about the samples of hydrogen

The volume and the pressure needed is instrument dependent and can vary greatly depending on the technique used to measure one compound. Therefore, the sample volume and pressure must be known and sufficient material must be collected.

7   References

[1] SO 14687-2 Hydrogen Fuel - Product Specification - Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles, 2012.

[2] 15NRM03, A2.2.3: Speciation method based on gas chromatography for the measurement of separate hydrocarbons in hydrogen

[3] GC-PDHID, report NPL

[4] 15NRM03, A2.2.1: Speciation method based upon cryo-focussed gas chromatography coupled with sulphur chemiluminescence detection for the measurement of separate sulphur-containing compounds in hydrogen

[5] "The fitness for purpose of analytical methods - A laboratory Guide to Method Validation and related topics (2nd ed. 2014), Eurachem Guide, B. Magnusson, U. Örnemark, ISBN 978-91-87461-59-0

[6] SO/CD 21087:2017, Hydrogen fuel - Analytical methods - PEM fuel cell applications for road vehicles

[7] ISO 6142:2015, Gas analysis – preparation of calibration gas mixtures – Part 1: gravimetric method for Class I mixtures

[8] ISO 6145: Gas analysis preparation of calibration gas mixtures using dynamic methods

[9] Methods of dealing with values below the limit of detection using SAS, US-EPA, C.W. Croghan, P.E. Egeghy

Standards:

ASTM D7941-14: Standard Test Method for Hydrogen Purity Analysis Using a Continuous Wave Cavity Ring-Down Spectroscopy Analyzer

ASTM D7653-10: Standard Test Method for Determination of Trace Gaseous Contaminants in Hydrogen Fuel by Fourier Transform Infrared (FTIR) Spectroscopy

ASTM D7649-10: Standard Test Method for Determination of Trace Carbon Dioxide, Argon, Nitrogen, Oxygen and Water in Hydrogen Fuel by Jet Pulse Injection and Gas Chromatography/Mass Spectrometer Analysis

ASTM D7892-15: Standard Test Method for Determination of Total Organic Halides, Total Non-Methane Hydrocarbons, and Formaldehyde in Hydrogen Fuel by Gas Chromatography/Mass Spectrometry

ASTM D7550-09: Standard Test Method for Determination of Ammonium, Alkali and Alkaline Earth Metals in Hydrogen and Other Cell Feed Gases by Ion Chromatography

ASTM D7607-11: Standard Test Method for Analysis of Oxygen in Gaseous Fuels (Electrochemical Sensor Method)

ASTM WK23815: New Test Method for Standard Screening Method for Organic Halides Contained in Hydrogen and other Gaseous Fuels, initiated 2009

JIS K 0123: JIS K 0123, General rules for gas chromatography/mass spectrometry, 2006.

JIS K0225: Testing methods for determination of trace components in diluent gas and zero gas, 2011.