Metrology for sustainable hydrogen energy applications

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

Task 2.3: Analytical procedures

Deliverable D4 (Recommendations report)

Recommendations report on optimized analytical protocols including fit-for-purpose analytical methods that enable the implementation of ISO14687-2

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Summary

One of the goals of the project 15NRM03 Hydrogen was to identify the current challenges in implementing ISO 14687-2 [1] in routine laboratory/analysis and to propose solutions to address these challenges. The challenges are at least twofold; firstly, the thresholds for some species are low and therefore challenging and secondly the total species cover a large number of species which are often difficult to analyse using one single analytical method.

In this report, we summarize all the outcomes of WP2 “Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO 14687-2 standard [2]”. As a conclusion, we propose solutions to address the identified challenges.

To tackle the challenges due to the numerous compounds to be analysed often at low levels, we review the current status of multi-components analysers and showed that they are a promising a promising way to reduce the number of analyses needed to assess the quality of hydrogen according to ISO14687-2 mostly due to the flexibility with these instruments.

To tackle the challenges encountered when analyzing “total species” methods, speciation methods for sulphur compounds, hydrogen chloride and hydrocarbons were developed and validated. These methods will allow determining which impurities among these families are actually present in hydrogen samples and may contribute to replace in the future the “total species” requirements in the standard by individual compounds.

Many analytical methods that are proposed for hydrogen purity testing need to be validated and conclusions on whether these methods are fit for purpose shall then be made following the criteria established in ISO/FDIS 21087 [3] Gas analysis – Analytical methods for hydrogen fuel – Proton exchange membrane (PEM) fuel cell applications for road vehicles. To perform these validations, it also requires certified reference materials.

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Acronyms for the analytical methods

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

1 - Introduction

The purity of hydrogen must comply with the tolerance limits set in ISO 14687-2:2012 [1a]: Hydrogen fuel – product specification – Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles. This standard specifies the quality characteristics of hydrogen fuel in order to ensure uniformity of the hydrogen product as dispensed for utilization in PEM fuel cell road vehicle systems. This standard is currently under revision as ISO/FDIS 14687 [1b] Hydrogen fuel quality – Product specification should be published in 2019. Currently, in EN17124:2018 [4] Hydrogen fuel — Product specification and quality assurance — Proton exchange membrane (PEM) fuel cell applications for road vehicles - specifications for nitrogen, argon and formaldehyde have been revised.

Table 1: Specifications for hydrogen purity

	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		2 except CH_4	including oxygenated organic species
Methane	-		100	
Oxygen	5		5	
Helium	300		300	
Nitrogen	100	N_2+Ar<100	300	
Argon	100	N_2+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	H_2S, COS, CS_2, mercaptans (NG)	0.004	H_2S, COS, CS_2, 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 Cl_2, organic R-X	0.05	HCl, organic R-Cl
Max. particulate conc.	1 mg/kg		1 mg/kg	

The description of the analytical methods required for such measurement is detailed in another standard; ISO/FDIS 21087 [3]: Gas analysis - Analytical methods for hydrogen fuel – Proton exchange membrane (PEM) fuel cell applications for road vehicles. In this standard, the validation protocol of analytical methods used for ensuring the quality of the gaseous hydrogen at hydrogen distribution bases and hydrogen fuelling stations for PEM fuel cells road vehicles is described. Recommendation on calculation of uncertainty budget is also provided.

One of the goals of the project 15NRM03 Hydrogen was to identify the current challenges in implementing ISO/FDIS 14687 in routine laboratory/analysis and to propose solutions to address

these challenges. The challenges are at least twofold; for once, the thresholds for some species are low and therefore technically challenging and the total species cover a large number of species which are often difficult to analyse using one single analytical method.

The following studies have been performed during the curse of the project:

1) A literature review of currently available impurity analysis methods using ASTM standards, JIS standards and in-house methods as sources documents has been performed

2) Discussions with multi-component instruments manufacturers in order to gather information about innovative methods under development were conducted

3) Discussions with instruments users to obtain information and feedbacks on implemented methods so far were conducted

4) Evaluation of the status of the methods from 1) and 2) in term of validation – what is done and what has to be done was performed

5) Methods were developed within the project targeting the total species i.e. “Total Sulphur”, “total halogenated”, “total hydrocarbons”

6) Analysis of real hydrogen samples using one of the method developed above in order to determine if other (organic) impurities not yet regulated in ISO 14687-2 are present in hydrogen

In this report, we summarize all the outcomes of the WP2 “Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO 14687-2 standard”. As a conclusion, we propose solutions to address the identified challenges.

2 – Literature review of current available analysis methods

In the report A2.1.1 “Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO14687-2 standard”, analytical methods were first presented for the following impurities: water, total hydrocarbons, oxygen, helium, nitrogen, carbon dioxide, carbon monoxide, total sulphur compounds, formaldehyde, formic acid and ammonia. Particles were not discussed in this report. The methods identified and described in the report have been either proposed in standards (US standards ASTM, Japanese standards JIS) or developed by National Metrology Institutes as NPL (UK), VSL (Netherlands) or RISE (Sweden). The outcomes are then summarized in two tables; first for each impurity and then for each analytical method. This last table is presented below (including some updates).

Table 2: Agreement between the impurity to be analysed and the techniques following the ISO requirements (green: ≤ the spec., orange: partially feasible or under development)

		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
Analytical technique	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

This is important to notice that information from this document needs regular updates as analytical methods for hydrogen fuel quality are constantly being developed and validated through different initiatives and projects mainly in Europe, Japan and USA.

From the table, it is clear that several methods have the advantages of analysing several impurities simultaneously. Among them, the GC-methods are promising methods for analysing impurities in hydrogen. It will however require combining several detectors and use of different GC columns.

Three techniques presented in this table, FTIR, OFCEAS, CRDS, correspond to analytical methods for which different providers propose multi-component instruments designed according to client´s specifications. A technique not mentioned in the table above and called Broad Tunable Laser (BTL) is also now proposed by a manufacturer (Blue Industry and Science) for hydrogen purity analysis for water, carbon dioxide, formic acid and formaldehyde.

3 - Discussion on multi-components analysers

FTIR, OFCEAS, CRDS and BTL characteristics have been assessed by consulting providers, reviewing literature and discussing with users of instruments. The outcomes were presented in the report “Assessment report of a multi-component analyser with optimized sampling analysis that meets the required detection limits as per business plans ISO/TC 197 and CEN/TC 268” which is the deliverable D3 of the project. It is important to notice that in this report, we considered analytical techniques that have the capacity to distinguish between the various components present and generate direct response of their presence and concentration (GC methods were therefore not discussed). After a short description of the analytical techniques, the performance assessment of these multi-components analysers as indicated by the instrument providers we contacted (one per technique) was summarised in a table presented below:

Table 3: Assessment of the performances of instruments enabling the simultaneous analysis of compounds mentioned in ISO14687-2 (green: feasible and ≤ the spec., orange: partially feasible (for example one or several compounds among "total species" or under development, red: not feasible, blue: currently under development)

	CRDS	FTIR	OFCEAS	BTL
Water	Instrument 1	Instrument 1	Instrument 1	
Oxygen	Instrument 4		Instrument 2	
Carbon dioxide	Instrument 1	Instrument 1	Instrument 2	
Carbon monoxide	Instrument 1	Instrument 1	Instrument 1	
Formaldehyde	Instrument 3	Instrument 1	Instrument 1	
Formic acid		Instrument 1	Instrument 1	
Ammonia	Instrument 2	Instrument 1	Instrument 1	
Helium				
Total nitrogen and argon				
Total hydrocarbons				
Methane	Instrument 1	Instrument 1	Instrument 1	
Ethane		Instrument 1		
Total sulfur compounds				
Hydrogen sulfide			Instrument 1	
Total halogenated compounds				
Hydrogen chloride	Instrument 5		Instrument 2	
Hydrogen bromide				
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 E. Smith	Blue Industry and Science, O. Le Mauguen
Volume/flow and pressure of gas needed	12 l/h	30-60 l/h	20 l/h	< 100 ml total, Low pressure

Using multi-component analysers is a promising way to reduce the number of analyses needed to assess the quality of hydrogen according to ISO14687-2 mostly due to the flexibility with these instruments. These instruments are often designed based on the client´s requirements; one of which is the selection of compounds to be analysed. In this way, every lab is free to select the compounds that cannot yet be analysed using other instruments available at the laboratory. There are currently only few users of the methods presented above. RISE has acquired two OFCEAS to analyse O2, CO, CO2, H2S and H2O, SINTEF (Norway) has through the H2Moves Scandinavia project documented the application of Long Path FTIR spectroscopy to hydrogen fuel quality control [5]. NPL (UK) has used CRDS LaserTrace 3, H2O module (Tiger Optic, US) for the determination of water in hydrogen.

To fully evaluate the potential of these techniques, it is important that external laboratories for example NMI (National Metrology institutes) perform a complete validation of the analytical methods using well established procedures and certified reference materials and/or comparative studies.

4 - Identified needs for further evaluation of performance characteristics of the methods

In this standard ISO/FDIS 21087 [3], the validation protocol of analytical methods used for ensuring the quality of the gaseous hydrogen at hydrogen distribution bases and hydrogen fuelling stations for PEM fuel cells road vehicles is described. Recommendation on calculation of uncertainty budget is also provided.

According to this standard, each laboratory shall verify the performance of the method against the fitness for purpose acceptance criteria of the standard before introducing them. If the method doesn't fulfil these criteria, it shall not be used for the analysis of impurities in H2; another method shall be used.

Therefore, we evaluated the current status of the analytical methods used for hydrogen purity assessment. Here again, it should be noticed that the information gathered need to be regularly updating taking into account the progresses reported in different projects.

In activity A2.1.2 of this project, available methods have been compared with regards to performance characteristics. Most of the information available for each method focused on the quantification limits since these are clearly challenging to reach. Other performances (i.e. repeatability, accuracy) are not always disclosed in standards, in users guides or specification guides provided by manufacturers or they are expressed so that direct comparison of the methods is not possible. Moreover, the methodologies followed to measure the reported performance characteristics are not clearly specified.

In the report A2.1.3 "Plan for the further development of analytical methods taking into account their performance characteristics", the information collected in the activity A2.1.2 have been summarized in order to discuss for each method which are the performance characteristics that require further evaluation. The results are presented in the following table.

Table 4: Identified performance characteristics among LOQ (Limit of Quantification), selectivity, working range, precision, trueness and ruggedness that requires further evaluation – green: performance characteristics evaluated and found "fit-for-purpose"; yellow: performance characteristics which need further evaluation but where some information is already available; orange: performance chracteristics needing evaluation

All the JIS and ASTM standards are referenced at the end of this document.

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

Based on the above table, none of the analytical methods currently available for hydrogen purity measurement can directly be 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. Therefore this report will provide guidance on method validation.

5 – Protocol for methods validation

As indicated in ISO/FDIS 21087, 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.

Method validation is the process used to confirm that the analytical procedure employed for a specific test is suitable for its intended use.

The validation of the method gathers experimental work performed to demonstrate that the method fits 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” [6]. Detailed information about validation process is also given in ISO/FDIS 21087 [3].

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 analysts will first need to acquire some tools (spiked materials, blanks, standards) and will then work through the validation process.

The table below (from report A2.1.3), summarizes the steps during the validation process.

Table 5: 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 analyte close to or below the expected LOD (n = 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	Visual examination 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) – n = 10 at a concentration preferably close to ISO/FDIS 14687 threshold	(abs. and rel.)	$b_{rel}\ \frac{\bar{x} - \mathrm{xref}}{\mathrm{xref}}$ x 100	calculate recovery $R(\%) = \frac{\bar{x}}{\mathrm{xref}}$ 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 times the limits proposed in ISO14687-2

6 – Criteria to be fulfilled before implementing a method according to ISO/FDIS 21087

Once the validation has been done, the conclusion on whether the method is fit for purpose can be drawn using criteria detailed in ISO/FDIS 21087. Criteria from the standard are gathered in the table below.

Table 6: Criteria to be fulfilled before implementing a method according to ISO/FDIS 21087

Parameters	Criteria
Detection limit/quantification limit	LOQ + u_{LOQ} (k=2) < threshold value
Working range	The higher value of the working range shall be at least equal to 2 times the threshold value
Selectivity (normal)	Interferences versus ISO/FDIS 14687 composition
Selectivity (extrem)	Interference versus critical situation observed in real situation
Precision	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 sulfur compounds)
Trueness	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 sulfur compounds)
Measurement uncertainties	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 sulfur compounds)

7 – Development and validation of speciation methods for the "total species"

To tackle the challenges encountered when analysing "total species" methods, three speciation methods were developed during the project for total hydrocarbons, total halogenated and total sulphur. Development of speciation methods (i.e. H_2S and COS instead of total sulphur) would allow measuring what the actual impurities are in the real samples of hydrogen. This could open the possibility in the future to suggest a replacement "total halogenated compounds" with the actual impurities.

7.1- Speciation method based upon cryo-focused GS coupled with SCD detection for the measurement of separate Sulphur-containing compounds in hydrogen

A speciation method to identify and quantify sulphur containing compounds in hydrogen based on cryo-focussing gas chromatography coupled with sulphur chemiluminescence detection has been developed and validated. Limits of detection have been calculated at around 0.25 – 1.21 nmol/mol for individual sulphur-containing compounds, which is significantly lower than the 4 nmol/mol threshold for "total sulphur compounds" (as specified in ISO 14687-2 [1]). The method is capable of measuring sulphur-containing compounds at pmol/mol concentrations ranging from heavy (tetrahydrothiophene) to light (hydrogen sulphide) molar mass compounds.

7.2 - Method for the measurement of HCl in hydrogen

The method is based on CRDS (cavity ring-down spectroscopy) using an OPO (Optical Parametric Oscillator) as light source. Dursan coated materials have been used in the flow system. As many different strong HCl absorption lines are available, the method is very robust and very insensitive to impurities. The system enables the measurement of HCl from the low nmol/mol to 100 µmol/mol (tested range: from 6 nmol/mol up to 46 µmol/mol) and more which is fully sufficient to comply with limit set in ISO 14687-2 [1] for total halogenated. It should however been noticed that too high HCl amount fractions may damage the CRDS mirror coatings.

7.3 - Speciation method based on gas chromatography for the measurement of separate hydrocarbons in hydrogen

A speciation method to quantify hydrocarbons based on the combination of two analytical techniques; (Gas Chromatography/Flame Ionisation Detector (GC/FID) and Thermal Desorption - Gas Chromatography/Flame Ionisation Detector – Mass Spectrometry (TD-GC/FID-MS) has been developed and validated. Measurement uncertainties have been calculated to be around 8-10 % for hydrocarbons with GC-FID and around 10-12 % for hydrocarbons with TD-GC/FID-MS. The limit of detection of 2 µmolC/mol for the "total hydrocarbons" (as required in the standard ISO 14687-2) has been shown to be achievable. The advantages of this method are that hydrocarbons as well as oxygenated compounds if present in the hydrogen can be identified either using the mass spectrometer for the TD-GC/FID-MS or the retention time for the GC/FID method. Even other organic compounds with a boiling point above 50 °C can be identified using the MS and quantified preferably using the FID. These include halogenated compounds as well as sulphur compounds. Depending on the volume of hydrogen sampled (for example 100 ml), the detection limit for these compounds is expected to be at least 10 nmol/mol.

8 – Analysis of real hydrogen samples in order to identify (organic) compounds not yet regulated in ISO/FDIS 14687

The method developed for the hydrocarbons (see 7.3) has been used for most of the hydrogen samples collected in WP1 of this project. The goal of this study was to assess the presence of

potentially harmful compounds (if any) detected in real hydrogen samples and not yet regulated in ISO 14687-2. The method allows the detection of organic compounds having boiling points in the range 50-350°C including organic sulphur compounds, halogenated organic compounds, hydrocarbons, oxygenated organic compounds (ketones, alcohols, esters, aldehydes). However, carboxylic acids could not be analysed due to the GC column that was used.

It is however important to notice that the transport times to the laboratory were often relatively long (from 2 weeks to little more than two months). The stability of the eventual impurities present in hydrogen is not known for a so long storage time and may be different depending on the inner material of the vessel and the sampling pressure. Some species present on the hydrogen may have therefore adsorbed onto the walls of the vessel. Therefore, no concentration is reported. To minimize adsorption risks, it is preferable to perform the sampling on sorbent tubes directly onsite.

Totally, 20 samples of hydrogen were analysed (10 samples produced from steam reforming and 10 samples from PEM water electrolysis).

The results show that very few compounds are present in the real samples of hydrogen analysed in this study. Moreover, the compounds were only found in one of the samples indicating that they are not common contaminants. Additional studies may be required to replicate the results and determine the significance and the origin of the compounds found.

The following compounds were identified in some of the hydrogen samples: cyclohexane (30-50 nmol/mol), propylene glycol (from 30 up to 300 nmol/mol), cyclohexanone (around 1000 nmol/mol in on sample) and cyclohexanone cyclic trimethylene acetal (around 100 nmol/mol). The propylene glycol can originate from liquid leak detector solution. It could have been introduced during the sampling procedure. Propylene glycol was the only compound that was found in two distinct samples.

HCl has not been found in any of the samples analysed (with a LOQ of 8 nmol/mol). Once again, it would however be interesting to complete these tests by analysing more samples using coated cylinders (which was the case for some of the samples analysed in this study) and after controlled transport times.

9 – Conclusion and future work

The challenges that laboratories face when implementing future ISO 14867 are at least twofold; firstly, the thresholds for some species are very low and therefore challenging and secondly, the total species cover a large number of species which are often difficult to analyse using one single analytical method. Another challenge is the number of impurities to be analysed in a single sample; at least 11 individual compounds and 3 families of compounds. No instrument is currently capable of performing all analyses required.

The literature review of currently available impurity analysis methods using as sources ASTM standards, JIS standards and in-house methods together with the discussions with multi-component instruments manufacturers and instruments users highlighted that there are many methods to choose between and that multi-component instruments are a promising way to reduce the number of analyses needed to assess the quality of hydrogen according to ISO 14687-2 mostly due to the flexibility with these instruments. However, the lack of a proper validation of these instruments has been pointed out in the report A2.1.3 of this project (see table 2**). It is therefore important that external independent laboratories as NMIs (National Metrology Institutes) perform a complete validation of the instruments using well established procedures and certified reference materials. In some case**

(i.e. total Sulphur, halogenated), it is critical to develop new certified reference materials to allow analytical laboratories to validate their internal methods or to propose strategy for method validation especially trueness.

The evaluation of the status of the methods from 1) and 2) in term of validation – what is done and what needs to be done clearly showed that many analytical methods that are proposed for hydrogen purity testing will need to be fully validated and conclusions on whether these methods are fit for purpose shall be made using the criteria established in ISO/FDIS 21087.

Methods validation is an ongoing work in different projects. ASTM published standards are validated for precision and bias by undergoing an inter-laboratory study program (ILS), in which the standard is tested by independent laboratories. In 2016, only one of the hydrogen standards has undergone an ILS (unfinished): ASTM D7653-10 (FTIR) (NH_3, CO_2, CO, CH_2O, CH_2O_2, H_2O).

During the course of this project, three analytical methods have been developed and validated:

- Speciation method based on gas chromatography for the measurement of separate hydrocarbons in hydrogen
- Speciation method based upon cryo-focused gas chromatography coupled with Sulphur chemiluminescence detection for the measurement of separate Sulphur-containing compounds in hydrogen
- Method based on CDRS for the measurement of HCl in hydrogen

During the project, a training course on method validation for hydrogen quality analysis was organized (International workshop – metrology for sustainable hydrogen energy applications, 7-8th of November 2018, France) for stakeholders and hydrogen industry. Another important aspect raised by this project is the need of regular training courses and workshops in order to validate analytical methods according to ISO/FDIS 21087.

Validation of some analytical methods according to ISO/FDIS 21087 is currently performed as part of the EMPIR project MetroHyVe (16ENG01).

Developing cost-efficient systems with focus on lowering operational costs is a possible solution for laboratories. This can be done for instance by coupling of several analytical techniques allowing the quantification of a relevant subset of compounds (for example critical parameters for a given production method). This approach is under investigation in the MetroHyVe project.

10 – References

[1] ISO 14687-2:2012 Hydrogen fuel – Product specification – Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles –

[2] ISO/FDIS 14687- Hydrogen fuel quality — Product specification. Revision of previous one and merge of all the ISO 14687 standards family

[3] ISO/FDIS 21087 Gas analysis – Analytical methods for hydrogen fuel – Proton exchange membrane (PEM) fuel cell applications for road vehicles.

[4] EN 17124:2018 Hydrogen fuel — Product specification and quality assurance — Proton exchange membrane (PEM) fuel cell applications for road vehicles

[5] Aarhaug, T.A. and Ferber, A.M.C., Deliverable 7.4 H2Moves Scandinavia

[6] 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

US 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

Japanese standards

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.