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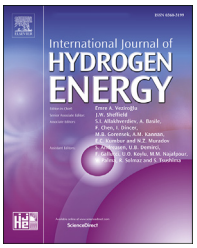

Assessment of hydrogen quality dispensed for hydrogen refuelling stations in Europe

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HIGHLIGHTS

- 10 samples collected from nozzle of public HRS in Europe.
- Standardized sampling methodology applied.
- All samples analysed by four laboratories = 40 analyses.
- Extensive evaluation of interlaboratory results.
- Discrepancies in H2 fuel violation depending on laboratory.

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ABSTRACT

The fuel quality of hydrogen dispensed from 10 refuelling stations in Europe was assessed. Representative sampling was conducted from the nozzle by use of a sampling adapter allowing to bleed sample gas in parallel while refuelling an FCEV. Samples were split off and distributed to four laboratories for analysis in accordance with ISO 14687 and SAE J2719. The results indicated some inconsistencies between the laboratories but were still conclusive. The fuel quality was generally good. Elevated nitrogen concentrations were detected in two samples but not in violation with the new 300 μmol/mol tolerance limit. Four samples showed water concentrations higher than the 5 μmol/mol tolerance limit estimated by at least one laboratory. The results were ambiguous: none of the four samples showed all laboratories in agreement with the violation. One laboratory reported an elevated oxygen concentration that was not corroborated by the other two laboratories and thus considered an outlier.

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Introduction

The number of hydrogen refuelling stations (HRS's) in the World is increasing fast; the number of public stations already passed 300 by the end of 2019. Quality control of the dispensed fuel requires the collection of a representative sample at the nozzle as recommended by ISO 19880-1 [1]. Due to high pressure, this is a demanding task: safety as well as integrity of the samples must be preserved. The purity requirements of hydrogen fuel are set by ISO 14687:2019 [2], in the following referred to as ISO 14687. In brief: the fuel index shall be higher than 99.97%, but high impact impurities like CO, sulphur and halogens should be limited to low amount fractions, 0.2, 0.004 and 0.05 μmol/mol respectively. Measurement of impurities in hydrogen fuels is a difficult task for analytical laboratories. Challenges on calibration, detection and preservation of such low level of impurities is still requiring trace analysis of reactive compounds. Therefore, the current number of analytical laboratories capable of performing analysis in accordance with ISO 14687 worldwide is low. The industry is therefore relying on less than 5 laboratories per area (i.e. North America, Europe and Asia). One challenge is to determine how comparable or reproducible the actual hydrogen fuel quality measurement reported to the industry is. The limited inter-laboratory comparisons conducted has the consequence of leaving little knowledge about the agreement in analytical results between laboratories. Now that hydrogen fuel quality is becoming part of regulation (European Directive 2014/94/EU), accurate and reliable hydrogen quality needs to be assessed from a fuel point of view and from a sampling and analysis point of view.

Impurities have sources from the production methods, but also the HRS itself and potentially the transfer of hydrogen to the HRS are sources of impurities introduced in the fuel [3]. ISO 14687 is focusing on conventional production methods and known impurity sources at the HRS. New production methods but also new storage methods [4] will require investigation to understand the potential new contaminants that could reach the fuel cell electric vehicle (FCEV). Evaluation of strategies for sampling from hydrogen stations have been done in [5,6].

The current number of analytical laboratories capable of performing analysis in accordance with ISO 14687 worldwide is small. Therefore, the inter-comparison and the quality assurance is at an early stage. Currently, a few limited inter-comparisons are ongoing worldwide through ASTM [7], EURAMET [8] or European projects like MetroHyVe [9]. Limiting to such activity is the lack of reference materials for at least five impurities at the tolerance limits given by ISO 14687.

Public dissemination of the quality of hydrogen fuel in Europe was started with the EU funded H2Moves Scandinavia project in 2012 [10]. This work was continued in the Fuel Cells and Hydrogen Joint Undertaking (FCH JU) funded project HyCoRA, running from 2014 to 2017 [11,12]. The project collected 28 gas samples, of which eight samples were in violation with the fuel quality requirement. The result is shown in Table 1: Oxygen and nitrogen were the most common violations observed [13]. For the HyCoRA project, there were no laboratories in Europe capable of analysing hydrogen fuel in accordance with ISO 14687-2:2012 at the time. Samples were therefore shipped to a laboratory in the US, Smart Chemistry, for analysis. The shipment of pressurized, flammable gas added significantly to the cost of the hydrogen fuel quality control. In addition, significant time from sampling to analysis was added by the overseas shipment as this normally took longer than two weeks.

Hydrogen fuel quality control data is regularly reported by NREL [14]. With more than 40 refuelling stations in operation in the state, California Department of Food and Agriculture has also reported results on hydrogen fuel quality [15].

As part of the FCH2 JU funded HYDRAITE project, a goal of establishing three laboratories in Europe capable of conducting hydrogen fuel quality control has been set. The project, running from 2017 to 2020 also aims at disseminating results showing the actual fuel composition dispensed by HRS's in Europe. This paper addresses the importance of quality control for laboratories analysing samples of hydrogen fuel. In contrast to the results in Table 1 where only one laboratory has been used, ten fuel samples will be analysed by four laboratories. The purpose of the exercise is to document the interlaboratory variance and to evaluate the implications for the compliance of the fuel quality.

Experimental

Gaseous sampling was conducted with a commercial adapter "Qualitizer" manufactured by Linde. This is a parallel sampling strategy, where a tee connector is inserted between the HRS

Table 1 – Results of HRS sampling in HyCoRA project. All concentrations in μmol/mol.* indicates outlying values being excluded from the estimate of mean. TS indicates total sulphur, TX indicate halogenated compounds, THC(C_1) indicates total hydrocarbons on C1 basis.The total number of samples is 28. N.A. indicates that mean could not be analysed from lack to quantified results.

	N_2	O_2	Ar	H_2O	He	CO_2	CO	TS	TX	CH_3COOH	HCHO	NH_3	THC (C_1)	CH_4
Tol	300	5	300	5	300	2	0,2	0,004	0,05	0,2	0,2	0,1	2	100
LOD	5	1	0,4	1	10	0,1	0,0005	0,0001	0,01	0,001	0,001	0,01	0,001	0,001
Mean	131	4,58	1,24	1,90	33,6	1,21	0,003	6,7E-05	0,01	n.a.	n.a.	n.a.	1,25	1,00
Mean*	32,6	3,51	1,24	1,90	33,6	0,312	0,003	6,7E-05	0,01	n.a.	n.a.	n.a.	0,19	1,00
ND	2	3	19	25	23	22	0	0	1	28	28	28	0	0
Violations	4	7	0	0	0	1	0	0	0	0	0	0	1	0
Max	1443	13	4,3	2,9	54	5,7	0,015	0,0004	0,028				30	17

nozzle and the FCEV receptacle. A sealed safety valve is installed for ensuring pressure to be kept below 87.5 MPa. A high-pressure hose connects the tee to a reducing valve rated for 103.4 MPa. The outlet pressure is reduced to a maximum of 16 MPa. The reducing valve is connected to a sample cylinder, typically a 10 L aluminium canister with DIN477/1 connector. Filling the cylinder is limited by a throttle valve. The valve is set as to fill the cylinder in approx. 3 min, approximately the time it takes to refuel a vehicle in accordance with SAE J2601 [16]. Because the adapter does not relay IR Communication information between receptacle and nozzle [17], refuelling is sometimes restricted to 60 MPa, depending on the HRS's non-comm protocol. After sampling, the sampling adapter is de-pressurized through a bleed-valve on the pressure regulator. The sampling adapter is illustrated in Fig. 1.

The sample cylinders used, were 10 L aluminium spectraseal from Linde with stainless steel valves. The use of passivation coating and stainless-steel valves was done as to minimize adsorption of fuel contaminants. The cylinders were prepared by three times repeating a cycle consisting of vacuuming to 1 mbar followed by pressurization to 10 bar with hydrogen 5.0. From the Smart Chemistry, pre-prepared Entek lined cylinders of 0.5–1 L volume were received. Sample transfer from the 10 L cylinders was conducted before the cylinders were sent to NPL and subsequentially ZSW and finally ZBT for analysis. The transfer was done with a 1/8" 316 stainless steel tube with a Linde HiQ Redline pressure regulator.

Ten gas samples were collected from HRS's in Germany, Sweden and Norway in February 2019. An overview of the samples analysed is given in Table 2.

Analytical methods

The analytical methods used by the laboratories are described in individual sections. For the European laboratories, compliance with ISO 21087:2019 [18] has been targeted. In brief, the standard does not set a specific analytical method requirement: The standard sets guidelines for testing the selected method's fit-for-purpose by evaluating the analytical performance of the selected method. ISO 21087 further set requirements for use of traceable reference materials and to conduct inter-laboratory comparisons.

Smart chemistry

Smart Chemistry is a private laboratory located in Sacramento, California. They have collaborated with ASTM to develop several methods for hydrogen fuel analysis. For total hydrocarbons, formaldehyde and organic halides ASTM D7892 was applied. The samples were pre-concentrated by a Cryo/Thermal desorption/Cryo sequence. Helium was analysed by GC-TCD in accordance with ASTM D1946. N_2, Ar, O_2, H_2O and CO_2 were analysed with GC-MS according to ASTM D7649. CO were analysed with GC-TCD according to ASTM D1946. Samples were cryo-focussed. Formic acid, ammonia, HCl, HBr and Cl_2 were analysed by GC-ElCD in accordance with ASTM

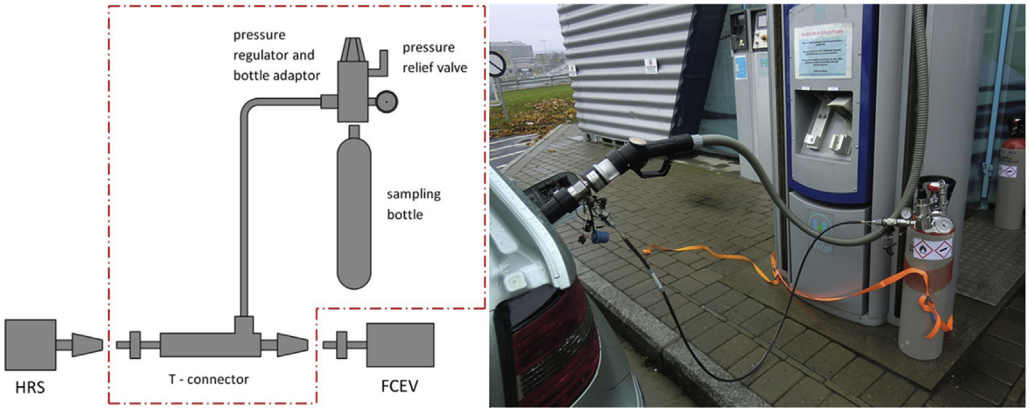

Fig. 1 – Schematic of parallel sampling (left) and actual refuelling with Qualitizer (right).

Table 2 – Table of HRS stations from which samples were collected (n.a.: information not available).

HRS	Date	Feedstock	Storage	ID
Bramfelder Chaussee, Hamburg (DE)	2019-02-06	SMR	Compressed	HD-SC1-1
Sachsendamm, Berlin (DE)	2019-02-07	SMR/BIO	Liquid	HD-SC1-2
Sachsendamm, Berlin (DE)	2019-02-07	SMR/BIO	Liquid	HD-SC1-3
Weiterstadt, Frankfurt (DE)	2019-02-08	n.a.	n.a.	HD-SC1-4
Wiesbaden (DE)	2019-02-08	n.a.	n.a.	HD-SC1-5
Mülheim an der Ruhe (DE)	2019-02-09	n.a.	n.a.	HD-SC1-6
Mariestad (SE)	2019-02-11	WE	n.a.	HD-SC1-7
Kjørbo (NO)	2019-02-15	WE	Compressed	HD-SC1-8
Kjørbo (NO)	2019-02-15	WE	Compressed	HD-SC1-9
Hvam (NO)	2019-02-20	WE	Compressed	HD-SC1-10

WK34574(v1). The samples were pre-concentrated by a Cryo/Thermal desorption/Cryo sequence. Total sulphur was analysed with GC-SCD in compliance with ASTM D7652. The samples were pre-concentrated with a Cryo/Cryo sequence.

National physical laboratory

The National Physical Laboratory (UK) is a national metrology laboratory and developed analytical methods to measure the hydrogen fuel contaminant listed in ISO 14687. The analyses were performed using NPL internal methods and accredited ISO 17025 for the following contaminants (N_2, O_2, Ar, CO, CO_2, CH_4, NMHC, total sulphur, H_2O, He). Nitrogen, oxygen and argon were analysed by gas chromatography (Agilent with pulsed discharge helium ionization detector (PDHID, VICI) using helium as a carrier gas. Water was measured using quartz crystal microbalance, QMA401 (Michell, US). Helium was measured using GC-TCD (Agilent Technologies, UK) using hydrogen carrier gas. Methane, carbon monoxide, carbon dioxide and non-methane hydrocarbons were measured GC (Peak Laboratories, US) coupled with a methaniser FID. Total sulphur compounds were measured by gas chromatography (Agilent, USA) with sulphur chemiluminescence detector (SCD 355, Agilent Technologies, USA). Organo-halogenated compounds were analysed using a TD-GC (Markes International, UK) coupled with mass spectroscopy (MS) with a split FID (Agilent Technologies, UK). Formaldehyde, formic acid and ammonia were measured by Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) (Syft, NZ). All analyses were calibrated using NPL gravimetric gas standards in hydrogen matrix gas. Gravimetric standards and/or dynamic standards (prepared by dilution using mass flow controller system (Bronkhorst, NL)) were used to generate calibration curve ranging covering the EN 17124 and ISO 14687 threshold and the measured values (as long as it is above the limit of detection). The data was scrutinised however no result was discarded without a technical reason. The calibration curve, results of analysis and uncertainties associated were determined using NPL software XLGENline [19]. An expanded uncertainty using a *k* value of 2 was used. In some cases, a more conservative uncertainty was derived from scientific experience.

Zentrum für Sonnenenergie-und Wasserstoff-Forschung

The Zentrum für Sonnenenergie-und Wasserstoff-Forschung (ZSW) is a German Landes-institute which developed its analytical capabilities according to ISO14687-2:2012 and is now adapting those methods to meet the needs of the current revision of the ISO and EN standards. The analyses were performed with internal methods. Argon, oxygen, nitrogen, methane, carbon monoxide and carbon oxide were measured by a pulsed discharge helium ionization detector (PDHID, VICI) after isothermal chromatographic separation (PerkinElmer LAS, Germany) using helium as a carrier gas. Hydrocarbons were quantified as the response of a direct FID without chromatographic separation (PerkinElmer LAS, Germany) using helium as a carrier gas and calibrated to C_1 with methane as reference substance. Total non-methane hydrocarbons (TNMHC) were calculated from the total hydrocarbon and methane levels by subtracting methane (PDHID) from the total hydrocarbon value. Helium was measured on a GC-TCD setup (Agilent Technologies) using argon as carrier gas. The same channel was used for plausibility checks of oxygen levels determined via GC-PDHID. Nitrogen and argon levels were determined by GC-TCD on its secondary channel using helium as carrier gas, again for an internal plausibility check of the primary setup's (GC-PDHID) quantifications. Total halogenated species were preconcentrated on a thermo desorber (TD) and measured by an electron capture detector (ECD) (both PerkinElmer, LAS Germany) which was calibrated to the response of trichloromethane using helium as carrier gas. Trichloromethane was used due to best locally available uncertainty budget of the calibration gas standard. The reference's response was broken down to Cl_1 equivalents. Total sulphur was determined in a similar way on the same gas chromatograph by diverting the sample to a flame photometric detector (FPD) (PerkinElmer LAS Germany) instead of the ECD. The detector was calibrated to the response of hydrogen sulphide. Water was determined on a dew point analyser working with a continuously measuring chilled mirror setup (Michell Instruments, UK). The relatively new continuously measuring method of optical feedback cavity enhanced absorption spectroscopy (OFCEAS) was used for quantification of ammonia, formaldehyde and formic acid (AP2E, France). On the OFCEAS setups, carbon monoxide and methane levels were additionally determined to cross validate the results of the analyses via GC-PDHID. Analytic devices were calibrated with locally available calibration gas standards. For calibration of the low levels of halogenated, sulphur, formic acid and ammonia, dynamic dilution via a critical orifice dilution system (CMC GmbH, Germany) was performed. The only exemption from calibration procedures in the case of formaldehyde and water, calibration and uncertainty budgets were used as supplied by the manufacturer, due to commercial unavailability of respective calibration gas in hydrogen matrix with a sufficiently low analytic tolerance. The entire gas path from sample vessels, calibration gas cylinders and dynamic dilution system to the respective analyser was set up with passivated gas lines to prevent adsorption or conversion of reactive species.

Results of the continuously measuring methods OFCEAS and chilled mirror were derived as the average from a minimum of 10 min of steady state and the respective channel's standard deviation over the evaluated segment. The reported values from repetition-based methods were derived from six repetitions by calculating respective species' averages and standard deviations of the measurements. The combined uncertainty budget from calibration curves, gas standards, results from the actual analysis and where applicable manufacturer certificates was taken into account with an expansion factor of $k = 2$.

Zentrum für BrennstoffzellenTechnik GmbH

Zentrum für BrennstoffzellenTechnik GmbH (ZBT) is one of the leading European research institutes for fuel cell and hydrogen technologies and a R&D partner in both European and national projects focusing on automotive applications and stationary power generation. In 2017, the ZBT started planning the expansion of the laboratory capacities in order to

acquire the ability to analyze hydrogen according to ISO14687-2:2012. Commissioning of the newly installed equipment was completed by beginning of 2020 except the analyzer for carbon dioxide, formic acid, formaldehyde, ammonia and halogenated species which has been sent back to the manufacturer for optimization. ZBT therefore performed the analysis beginning of 2020 with three of four analyzers. A 4-channel gas chromatograph equipped with plasma emission detectors (GC-PED) was used for the analysis of methane, carbon monoxide, oxygen, argon and nitrogen. The separation was isothermal and helium was used as the carrier gas. The amount of total sulphur was determined using a gas chromatograph (GC) equipped with a sulphur chemiluminescence detector (SCD). Due to the low limit, these samples were previously concentrated using a thermo desorber (TD) and a quantification limit of 0.0002 μmol/mol could be reached. The detector was calibrated with hydrogen sulfide and the total sulphur was determined as the equivalent. The hydrogen sulfide calibration standard was diluted by mass flow controller system to the level of the 14,687 threshold value. A Quartz Crystal Microbalance analyzer (QMC) was used to analyze the water content. The calibration was carried out using an internal standard (moisture generator). Certified calibration standards in hydrogen matrix were used for calibration. All instruments, pipelines and components were purged with hydrogen quality 6.0 during measuring breaks in order to prevent entries of minimal contamination.

Statistical test

To determine if there is a systematic difference between two datasets (in this case, two laboratories) a statistical test was used: paired sample *t*-test [20]. The test will determine if there is a significant difference between the dataset produced by two laboratories at the 95 % confidence level. Paired sample *t*-test was performed between the laboratories for water and nitrogen amount fraction. For each measurement, the three laboratories were compared to the NPL or ZSW laboratory by calculating the difference between the measured value and the NPL or ZSW laboratory. The mean of the difference between the NPL or ZSW laboratories and the other laboratory was established with the standard deviation of the mean of the difference using the ten hydrogen fuel samples. The paired test *t*-test value is then determined as defined below:

$$t = \frac{\overline{|d|}}{s_d/\sqrt{n}}$$

where s_d is the standard deviation of the difference d; n is the number of observations used in the statistical test; d is defined as $d_i = a_i - b_i$.

Where a_i and b_i are the independent measurement of lab A and lab B on sample i with lab B considered as the reference.

Then the paired sample *t*-test is compared to the *t*-test value at 95% confidence level with a degree of freedom equal to n-1.

Results and discussion

The ten samples were analysed by European laboratories and Smart Chemistry shortly after sampling. Only four of the

Table 3 – Analytical results for four samples. All results in μmol/mol. SC indicates Smart Chemistry.

	HD-SC1-1				HD-SC1-4				HD-SC1-6				HD-SC1-7			
	SC	NPL	ZSW	ZBT	SC	NPL	ZSW	ZBT	SC	NPL	ZSW	ZBT	SC	NPL	ZSW	ZBT
N_2	75	70 ± 11	82.6 ± 4.7	79.42 ± 10.77	237	231 ± 22	198.4 ± 11.2	203.67 ± 8.82	8.9	7.96 ± 0.42	15.5 ± 1.7	12.87 ± 0.96	234	33.5 ± 1.8	33.87 ± 1.9	70.26 ± 6.8
O_2	<1	0.794 ± 0.023	4.55 ± 0.27	0.0267 ± 0.0071	1.1	<0.030	1.01 ± 0.05	0.054 ± 0.0126	2.3	1.105 ± 0.033	1.19 ± 0.44	0.0169 ± 0.0034	<1	<0.030	0.39 ± 0.06	0.0675 ± 0.00144
H_2O	<1	3.30 ± 0.20	3.98 ± 0.30	5.64	<1	4.29 ± 0.30	4.73 ± 0.24	5.93	1.5	6.01 ± 0.40	9.62 ± 0.55	NM	<1	7.1 ± 0.5	8.25 ± 0.49	11.81

samples contain contaminant information above detection level that is discussed in this paper. The results of these samples are given in Table 3. Results of all samples are available in the additional materials provided (see Supplementary materials).

The results of the different laboratories were discussed first in order to establish the presence of outliers or measurement issues within some of the laboratories or samples. After the comparison of laboratory performance on the ten different samples of the sampling campaign, the results will be discussed in term of hydrogen fuel quality.

Inter-laboratory results comparison

Hydrogen fuel laboratory inter-comparisons are a limited exercise with only few compounds tested in the past years [21]. Moreover, the current state of the art only allows testing of a limited range of contaminants, due to the lack of a commercially available, traceable gas standard at trace gas levels. For ammonia, formaldehyde, formic acid, halogenated compounds and total sulphur, reference materials in hydrogen at ISO 14687 threshold level are not commercially available. Therefore, exchange of real hydrogen fuel samples was used as alternative methodology to compare laboratory performance bearing in mind that the stability of the impurity in the cylinder is not guaranteed. A difficulty in interpreting inter-laboratory comparison is when measurement uncertainties from all participant are lacking. It may provide bias in statistical test showing significant difference between two participants while the difference is only the uncertainty of their measurement. An example of this aspect can be done on the nitrogen amount fraction measurement for HD-SC1-4, the four laboratories provided results within 198–237 μmol/mol. Observers may consider it as a significant difference (reaching approximately 39 μmol/mol), however when taking into consideration the measurement uncertainties of the participant, the results agrees on 95% confidence level. Therefore, the difference between the laboratory can be considered as part as the measurement error inherent to each laboratory. Without the measurement uncertainty, an observer would be unable to determine which laboratory results are comparable or significantly different.

Water

For water, there is significant difference between Smart Chemistry and EU laboratories. The EU laboratories show elevated water concentration in all samples. Only for sample HD-SC-1-7 was the three EU laboratories in agreement with a concentration above the 5 μmol/mol tolerance. For the other samples the results were inconclusive. The Smart Chemistry results generally showed low water concentrations: only for sample HD-SC-1-6 was a concentration above LOD estimated. The analytical results for water for all samples is shown in Fig. 2. Smart Chemistry shows lower results for all samples. The EU laboratories show good consistency for samples HD-SC-1-2, HD-SC-1-3, HD-SC-1-8, HD-SC-1-9 and HD-SC-1-10. Not considering the result from Smart Chemistry, only sample 6 and 7 can be concluded to be outside of the tolerance limit of 5 μmol/mol.

A paired comparison was performed between NPL, ZSW and ZBT laboratories. The results showed that NPL results are significantly different from the two other laboratories at 95% confidence level. The results from NPL were lower than the two other laboratories. Considering that NPL and ZBT are using the same technology (quartz crystal microbalance), it is unlikely that there is a technology bias therefore it suggests that the calibration gas or standards used could be the source of the bias. Without an additional gas reference, it is difficult to determine which laboratory results are the most accurate. The two other EU laboratories (ZSW and ZBT) were not significantly different at 95% confidence level. The US laboratory is significantly different from the three EU laboratories at 95% confidence level. Reference material for water amount fraction in hydrogen within 2–7 μmol/mol would be critical to evaluate what the explanation of the significant bias between the Smart Chemistry, NPL and the two other EU laboratories.

Nitrogen

Quantifiable nitrogen levels were estimated for all samples but did not in conflict with the 300 μmol/mol threshold level. The analytical results for nitrogen for all samples is shown in Fig. 3. Whereas the laboratories showed good correlation for most samples, a significant deviation was observed for sample HD-SC-1-7. With three laboratories showing good correlation on HD-SC-1-7, the result from Smart Chemistry was tagged as an outlier and therefore excluded from the paired comparison statistical test. From the paired comparison statistical test, two EU laboratories agreed (NPL and ZSW) at 95% confidence level. On the other hand, Smart Chemistry showed a significant difference with NPL on 95% confidence level even if the difference is small on average (average difference between NPL and Smart Chemistry is below 2 μmol/mol). The other EU laboratory ZBT showed significant difference on the paired comparison test with ZSW and NPL at 95% confidence level. The values reported by ZBT are significantly higher than the values reported by the two other EU laboratories.

Oxygen

Quantifiable nitrogen levels were estimated for all samples but did not in conflict with the 5 μmol/mol threshold level. The analytical results for nitrogen for all samples is shown in Fig. 4. For sample HD-SC-1-1 an outlying value was identified from ZSW. For sample HD-SC-1-6, an elevated water level was estimated by three laboratories. Generally, SC reported with the exception of two samples, higher oxygen estimates than the other laboratories. This can be ascribed to the fact that the laboratory LOD was higher for SC than the other laboratories. Because oxygen was only quantifable in 19 samples, a paired *t*-test could not be conducted.

Comparison of value close to limit of detection and much lower than threshold levels of ISO 14687

The comparison of the laboratory performance was done for all gaseous compounds measured. However, it should be noticed that in some case, the actual amount fraction present in the sample was significantly lower than the ISO 14687 threshold. In this case, laboratories may be quite distant from the normal measurement range and its calibration curve thus

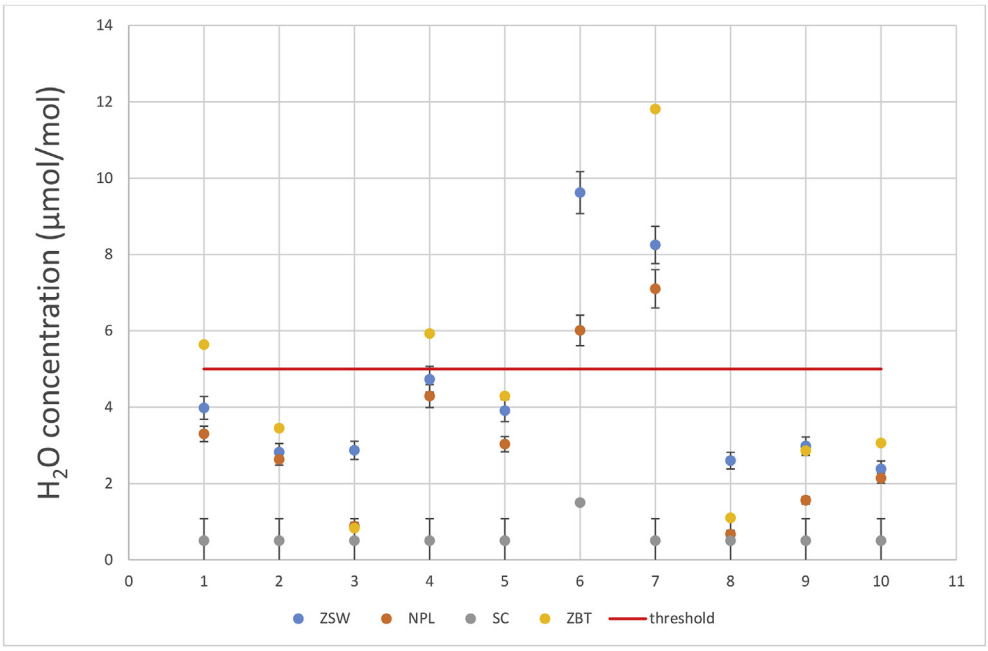

Fig. 2 – Water concentrations estimated for all samples.

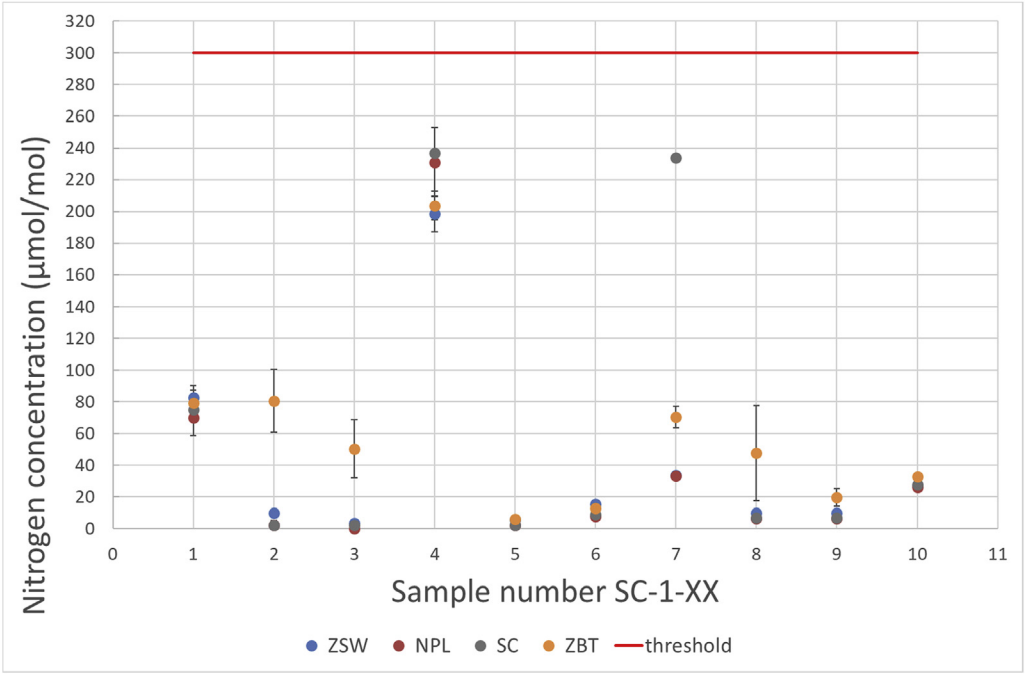

Fig. 3 – Nitrogen concentrations estimated for all samples.

extrapolation may be performed. In the situation of methane, helium and argon, the discrepancies or agreement provide low information on the measurement accuracy around the ISO 14687 threshold, however, it may indicate a difference in limit of detection determination.

Methane. It should be noted that methane amount fraction in all samples was much lower than the ISO 14687 threshold and therefore did not provide significant information on the methane accuracy measurement at 100 µmol/mol. The measurement of methane showed a good agreement between the

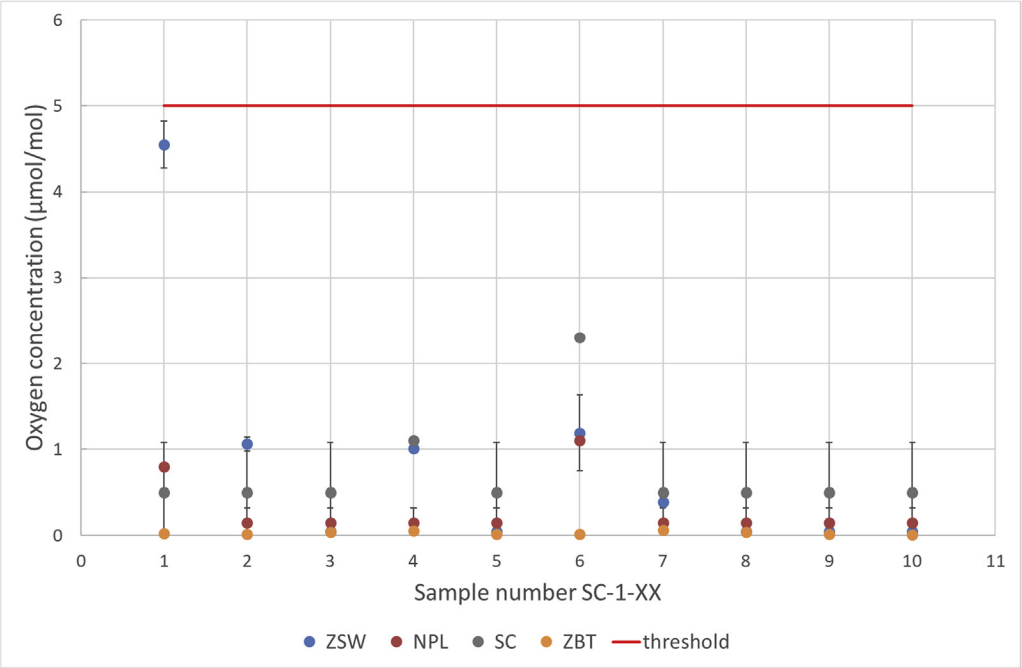

Fig. 4 – Oxygen concentrations estimated for all samples.

three European laboratories. ZSW did not detect any methane above their analytical method detection limit, which is in agreement with the results from ZBT and NPL. ZBT and NPL results agrees especially for HD-SC1-7 and HD-SC1-10. These two samples were reported by both laboratories in the 0.02 µmol/mol range with agreement on 95% confidence level. The US laboratory results differ significantly on 6 samples (HD-SC1-1, −4, −6, −7, −8, −10) from the EU laboratories. As mentioned above, the discrepancies provide low information on the measurement accuracy around the ISO 14687 threshold, however, it may indicate a difference in limit of detection determination.

Helium, argon. As reported for methane, the measured values by the laboratories were more than 100 times lower than the threshold level. Differences were observed between laboratories close to their limit of detection. It would be scientifically interesting to discuss the determination of the limit of detection, however it provides little information on the ability of the laboratory to perform accurate measurement of helium and argon close to the ISO 14687 threshold.

Carbon monoxide. While most EU laboratories reported carbon monoxide values below their limit of detection, Smart Chemistry was reporting values for most samples. It would be interesting to investigate the determination of the detection limit even if there is agreement between laboratories.

Determination of "total" and results comparison

The determination of the total sulphur, halogenated, and hydrocarbons is complex as different methodologies are applied. In these cases, comparing laboratory performance is delicate as it may be strongly method dependent (i.e. list of compounds quantified versus total method). As continued work on validation at ZSW showed, the TD-ECD and TD-FPD methods are potentially prone to high uncertainties, because of species specific response factors: A species which was used as calibrant to represent the most probable contamination of its type, might lead to a misquantification of a different species of the same "total" group, due to a differing response factor at the same concentration level in the sample. In this particular case, the effect might primarily be attributed to differing adsorption behaviour of species at −30 °C at the TD unit's adsorbent bed. These new findings, led to a change of setups to summation of contents of specific species after chromatographic separation, now at the risk of omitting contribution from species, which may not pass the chromatographic column within a reasonable time for analysis.

Total hydrocarbons excluding methane. The three EU laboratories reported results for all the samples below their detection limit. Smart Chemistry results disagreed with them as it reported values above the limit of detection of all EU laboratories for all samples. It highlights two points: is there a significant difference in the limit of detection determination or is there a difference due to the analytical method used? The European laboratories were measuring directly total hydrocarbons based on the flame ionization detection (direct or using conversion of all hydrocarbons into methane through methaniser) while the US laboratories was speciating and quantifying a list of more than 50 hydrocarbon compounds. The summation of these compounds was used to determine the total hydrocarbons values. The two different approaches may be one of the reasons of the disagreement.

Total sulphur. Two European laboratories (ZSW and NPL) and Smart Chemistry agree on the total sulphur measurement for all samples. The US laboratory reported the lowest value while the two EU laboratories reported below their limit of detection (higher than the reported value from the US laboratories). Only one European laboratory reported a value above the three other laboratories results and even a value above the ISO 14687 threshold.

Halogenated compounds. Halogenated compounds have not been reported by European laboratories. Smart Chemistry has consistently reported tetrachlorohexafluorobutane in samples over many years [11,12]. The revised ISO 14687 places a heavy focus on chlorinated compounds but defines a generalized report on "halogen ion" basis. Concentrations reported have not been in violation with the ISO threshold of 0.050 μmol/mol as reported on a molecular basis. If recalculated to a single chlorine ion basis by multiplication by four for the chlorine count, there have been many violations in the past. For this particular dataset, two out of ten concentration estimates for freon was on a HCl basis and in violation with the ISO tolerance limit. Taking the six fluorine equivalents per molecule of the freon into account, the results would account for additional six violations of the ISO threshold limits. This ambiguity of formulation leaves room for interpretation, as fluorinated species are usually not considered an issue for a fuel cell but would formally have to be taken into account.

The European laboratories were unable to detect chlorinated compounds or tetrachlorohexafluorobutane with limit of detection lower than 0.001 μmol/mol at NPL. With NPL claimed limit of detection, it should have been detected in all the samples to be in agreement with Smart Chemistry. The detection and quantification of tetrachlorohexafluorobutane should be studied and the method compared as there is a clear discrepancy on this compound which represents the main sources of halogenated compounds in hydrogen fuel according to Smart Chemistry.

Comparison of results on reactive and potentially unstable compounds. Formic acid, ammonia and formaldehyde are reactive compounds and their lifetime in a metal cylinder is uncertain. Therefore, inter-laboratory comparison should be conducted where sample stability should be investigated. Moreover, it is extremely rare to detect and quantify one of these compounds in real hydrogen samples.

Formic acid. All laboratories agree with results below their limit of detection except for one sample (HD-SC-1-1). NPL was the only laboratory to report a value above the limit of detection of all laboratories. As it was not detected by the laboratory, it would require additional investigation upon the potential interference on their analytical method. As NPL is using a new analytical technology SIFT-MS, it is possible that undocumented interference has happened.

Formaldehyde, ammonia. All the laboratories reported values under the limit of detection of their own methods. Therefore, all the laboratories agree but it does not demonstrate that the four laboratories can measure accurately formaldehyde or ammonia at the ISO 14687 threshold. To demonstrate this, an inter-laboratory comparison sample should contain a measurable amount fraction of formaldehyde or ammonia which is currently unavailable commercially.

Inter-laboratory comparison using real hydrogen fuel samples. This exercise showed good agreement overall between Smart Chemistry and the EU laboratories with only few cases of disagreement around the ISO threshold value (only for water measurement).

However, it highlights the complexity to use real hydrogen fuel samples for inter-laboratory comparison because.

- most of the real hydrogen fuel samples did not contain any impurities or at low amount fraction (10–100 times below ISO threshold). Therefore, the laboratories are comparing performance slightly outside of the range of interest of the industry.
- Stability of the real hydrogen fuel samples is unknown and shared between participants. Analyses are performed over long period of time and changes may occur especially for the reactive compounds (e.g. ammonia, formic acid, formaldehyde)

Nevertheless, the benefit of such inter-comparisons can be shown especially in the case of systematic differences (i.e. a laboratory consistently reporting lower or higher on all samples). In the absence of inter-laboratory comparisons with sufficiently contaminated samples, it allowed to identify possible bias on water measurement from the Smart Chemistry.

Hydrogen fuel quality in Europe – results of the sampling campaign

The analysis of the samples showed that six samples were in compliance with the ISO 14687 requirements and with no elevated impurity concentrations were noticed by any of the four laboratories.

Four samples (HD-SC1-1, HD-SC-1-4, HD-SC-1-6 and HD-SC-1-7) showed quantifiable results on nitrogen, oxygen, water and sulphur. Moreover, three samples (HD-SC-1-4, HD-SC-1-6 and HD-SC-1-7) showed results for water from at least one laboratories above the ISO 14687 threshold as shown in Table 3. It is important to investigate these discrepancies as detailed in the previous part of the discussion. For water, one EU laboratory (ZBT) found the three samples above the ISO 14687 threshold while Smart Chemistry did not measure any water above 2 μmol/mol. The two other EU laboratories (NPL and ZSW) showed closer agreement in their results with HD-SC1-1 and HD-SC-1-4 compliant with ISO 14687 threshold while HD-SC-1-6 and HD-SC-1-7 were not compliant. It was decided that only the samples HD-SC-1-6 and HD-SC-1-7 were not compliant with ISO 14687 threshold.

After such an extensive exercise involving four laboratories, 40 measurement results and 7 independent violation of

Table 4 – Results from sampling showing mean, individual tolerance violations (# results), analyte not detected (ND), analyte not analysed (NA), maximum value, number of sample tolerance violations (# > Tol) and number of sample tolerance violations reported by at least 50% of the laboratories (# > 50%).

Impurity	ISO 14687:2019	Mean	> Tolerance	ND	NA	MAX	# > Tol	#> Tol 50%
H_2O	5	3.9	7	9	1	12	4/10	2/10
Total non methane Hydrocarbons	2	0.23	0	30	0	0.58	0/10	0/10
CH_4	100	0.076	0	19	0	0.41	0/10	0/10
O_2	5	0.76	0	21	0	4.6	0/10	0/10
He	300	14	0	28	10	15	0/10	0/10
Ar	300	0.58	0	25	0	2.0	0/10	0/10
N_2	300	55	0	4	0	237	0/10	0/10
CO_2	2	0.11	0	27	10	0.26	0/10	0/10
CO	0.2	0.010	0	29	1	0.045	0/10	0/10
Total sulphur compounds	0.004	0.00073	1	21	1	0.0044	1/10	0/10
HCOH	0.2	0.017	0	29	7	0.063	0/10	0/10
HCOOH	0.2		0	32	8		0/10	0/10
NH_3	0.1		0	32	8		0/10	0/10
Halogenated compounds	0.05	0.014	2	20	10	0.047	2/10	0/10

ISO 14687:2019 threshold, only two samples were considered in violation of ISO 14687:2019 assuming that the violation is corroborated by more than one laboratory. In a real case scenario, the analyses are performed by only one laboratory. Therefore, depending on the laboratory performing the analysis, it could have led by HRS closure due to false positive or contamination of FCEV due to undetected contaminant above threshold.

Aggregated results from the sampling is given in Table 4. The table give information about the quantifiable results obtained from analysis. The main culprit is water: with a mean value close to the 5 μmol/mol tolerance based on 30 analytical results and with a maximum value of 12 μmol/mol. Violations of tolerance were limited to four samples (HD-SC1-1,4,6,7) but only two samples (HD-SC1-6 and HD-SC1-7) had the violation corroborated by two or more laboratories.

Impurity origin discussion

Quantifiable nitrogen levels not in conflict with the 300 μmol/mol threshold level were estimated for all samples. Oxygen did not show any violations, but elevated results were estimated by individual laboratories (HD-SC-1-1 ZSW and HD-SC-1-6 SC). As discussed previously, no correlation between nitrogen and oxygen amount fraction were observed which indicate that the nitrogen value is not correlated to air intake during actual sampling or presence in the sampling system's dead end due to insufficient bleeding before filling the cylinder.

From the contaminants quantified (mainly water and nitrogen), there was no trend with the hydrogen production method. No significant difference was observed between hydrogen from SMR origin (HD-SC-1-1 to −3) and hydrogen from water electrolysis origin (HD-SC-1-7 to 1–10). It demonstrates that the overall hydrogen quality at the HRS is not significantly different depending on the hydrogen feedstock.

Therefore, the presence of impurities like nitrogen and water in the hydrogen fuel may originate from production batch differences (within the ISO 14687:2019 tolerance) or from maintenance operation (i.e. inerting system with nitrogen for maintenance operation).

Conclusions

Assessment of hydrogen fuel quality dispensed from HRS's in Europe shows that the fuel quality is generally good and conforming to international quality standards. Only elevated concentrations of nitrogen, oxygen and water were observed. Four samples had concentration estimates outside the ISO 14687 fuel tolerance: EU laboratories were conclusive for two of these samples: for the other two it could not be concluded whether the samples were outside the tolerance given by ISO 14687.

Some contrast in results between laboratories are observed. According to Smart Chemistry all samples are within specification. The EU laboratories are better correlated with each other than Smart Chemistry. It demonstrates the importance of laboratory comparison, availability of preferably traceable reference materials, quality control and method validation. This is likely to be the result of the efforts in HYDRAITE and other EU funded projects (e.g. MetroHyVe) to provide reference materials and to conduct further round-robin testing at laboratories in Europe.

The results are consistent with earlier results from HyCoRA in reporting nitrogen, oxygen and water as the main impurities found in hydrogen dispensed from refuelling stations in Europe. However, since Smart Chemistry appear to be reporting low estimates compared with the three European laboratories, it is plausible that the violations of the water content in the dataset of Table 1 could be present but undetected.

This work has shown that using real samples from HRSs for round robin testing is viable for impurities that can normally be detected in hydrogen fuel: nitrogen, oxygen and water. Statistical evaluation of the results were able to identify significant differences between laboratories (NPL and ZSW vs. ZBT for water, and ZBT vs. NPL, ZSW for nitrogen). Since the true value of the samples are unknown, only identification of significant differences could be made. The identification of the significant differences would help laboratories achieving more accurate and comparable hydrogen fuel results.

This work illustrates the importance of laboratory quality assurance. By having four laboratories analyze the same samples, variance between the laboratories that would lead to different conclusions with respect to ISO 14687 compliance have been identified. For HRS operator fuel compliance to be ensured, contracting several laboratories is not an option from a cost perspective. Therefore, quality assurance of laboratories must be ensured in order to have correct results from HRS fuel quality audits.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2020.11.163.

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