Hydrogen quality sampling at the hydrogen refuelling station – Lessons learnt on sampling at the production and at the nozzle.

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3 - 5 Highlights (85 characters):

- Recommendation on H2 fuel sampling for production process and H2 refuelling station
- Experimental results on hydrogen contaminant purging procedure at hydrogen refuelling station
- Contaminants (O2 and H2O) above ISO 14687 values due to improper sampling procedure
- Linde H2 Qualitizer procedure allows H2 sampling at HRS (35&70 MPa NWP dispensers)
- H2 Qualitizer procedure suitable for reliable hydrogen sample (no air contaminant)

Abstract

Fuel cell electric vehicles and hydrogen refuelling infrastructure are developing quickly in Europe, the USA and Asia. Hydrogen quality for transport applications requires compliance with ISO 14687-2: 2012 and EN 17124:2018 - this needs representative sampling, at the hydrogen production process and at hydrogen dispenser nozzle (which typically fill vehicles to a Nominal Working Pressure of either 35 or 70 MPa). The low thresholds in ISO 14687-2 for oxygen and water can be exceeded if the sampling procedure fails to purge the system sufficiently, which would lead to false results (60% in this study). Purging requirements to remove water were studied using a low pressure sampling rig. For hydrogen dispenser sampling using the Linde H2 Qualitizer (suitable for dispensing pressures up to 70 MPa), purging number and the effect of the initial fill level of a vehicle compressed hydrogen storage system were investigated experimentally to avoid hydrogen quality violation due to oxygen false positive. The study procedure reduces from 60% to 0% hydrogen quality violation. The next challenges highlighted are safe purging and reliable sampling of reactive contaminants in gas cylinders.

1. Introduction

The deployment of fuel cell electric vehicles (FCEV) is accelerating globally. Across Europe, countries have initiated national policies to introduce hydrogen mobility technologies to the market over the next few decades. According to the European Commission, hydrogen could represent 32% of the European fuel mix in 2050 [1]. The European hydrogen market is anticipated to increase significantly over the few next years (current proposals are as follows; France: 100 hydrogen refuelling stations (HRS) by 2023, 400-1000 by 2028 [2]; Germany: 100 HRS in 2019 and 400 by 2023 [3]; the Netherlands: 50 HRS by 2025 [4] and UK: 20 HRS by 2020 [5]).

Fuel cell electric vehicles have strict requirements in terms of hydrogen fuel quality. Thirteen gaseous contaminants and particulates must be monitored according to international standards ISO 14687-2 [6], SAE J2719:2015 [7] and EN 17124 [8]. The presence of these contaminants can reduce the lifetime of fuel cells [9] and of the FCEV. It is therefore crucial for users and producers to ensure that contaminants in hydrogen are measured accurately. According to the European Directive 2014/94/EU [10], there is a requirement for hydrogen supplied to FCEV to be of a suitable quality (i.e. compliance with ISO 14687-2). This involves reliable purity testing and sampling to show that none of the threshold limits for the 14 impurities specified in ISO 14687-2 [6] are exceeded. It is critical to perform reliable and representative sampling of the hydrogen fuel at the HRS nozzle and, where applicable, at other points closer to the production process as part of a hydrogen quality control plan. Considering the low threshold for oxygen (5 µmol/mol) and water (5 µmol/mol) in the hydrogen fuel standard ISO 14687-2 [6], the risk of contamination due to an air leak or improper purging may lead to false positives [11]. Hydrogen fuel is typically present at various pressures within an HRS, depending on the use of an on-site production process, delivered hydrogen (e.g. in tube trailers), high pressure storage banks and the filling pressure(s) at the nozzle of the HRS. Hydrogen for road vehicle applications is typically delivered at pressure up to 43.8 or 87.5 MPa (for a 35 MPa or 70 MPa Nominal Working Pressure (NWP) in the vehicle. Such high-pressure sampling represents an analytical and technical challenge in order to operate safely and obtain a reliable sample for all the contaminants in ISO 14687-2.

The recent draft standard ISO/DIS 19880-1 offers guidance for the sampling of dispensed hydrogen so that gas phase contaminants may be captured and taken off site for laboratory analysis [12]. Representative samples from multiple fuelling station hydrogen storage banks, where applicable, should be taken to confirm that all storage banks have been properly cleaned and purged to assure compliance with the ISO 14687-2 fuel cell grade hydrogen impurity threshold limits [12]. Depending on the type of hydrogen supply (offsite or onsite), ISO/DIS 19880-1 mentions that sampling may be conducted upstream of the fuelling nozzle as part of a hydrogen quality control plan to the extent that no changes occur to the quality of hydrogen [12]. Sampling from a production process may be required in order to check the supply chain (i.e. where the hydrogen producer is different from the HRS operator), to monitor a specific subset of contaminants, or to perform hydrogen sampling at lower pressures (for instance where there may be less constraints than when sampling at higher pressures). The draft standard for hydrogen fuel quality control (ISO/DIS 19880-8) [13] may require an HRS operator to perform risk assessment on the probability of the presence of each contaminant in hydrogen fuel. In order to justify the final risk assessment, analysis at different points of the process may be required [14]. There may be a need to obtain representative hydrogen fuel samples at the hydrogen production process (i.e. steam methane reforming or PEM water electrolyser) which involve sampling at pressures between 1 to 8 MPa. No standardised procedure is currently available for hydrogen sampling at low pressure.

Based on the guideline of ISO 19880-1 mentioning that representative samples should be considered utilizing hydrogen from all hydrogen banks at fuelling station, it is important to follow the fuelling protocol in order to obtain a representative sample from all the hydrogen banks. Sampling of gas and particulate samples from 70 MPa hydrogen dispensers is challenging mainly due to the high pressure involved. The fuelling protocol according to SAE J2601:2016 dictates a test pulse of up to 87.5 MPa to precede fuelling [15]. This implies that sampling instrumentation must be pressure rated for 103.4 MPa (15,000 psi). These requirements limit, and severely increase the cost of, hardware to be used for sampling [16].

ASTM D7606 describes a sampling apparatus for hydrogen fuel at 70 MPa [17]. The sampling procedure requires a large purge of hydrogen (1 kg of hydrogen) through the sampler and the sample gas cylinders. Therefore, an exhaust gas tube (vent line) is mandatory for this large purging due to health and safety reasons. SINTEF [18] and a US laboratory [19] have used this kind of instrumentation previously for HRS quality monitoring. Whereas the purging option is beneficial, there is an HSE aspect of venting large amounts of hydrogen from the HRS [16].

The H2 Qualitizer allows for sampling of hydrogen from the HRS without needing to override safety elements of the control system, or without needing excessive venting of hydrogen from purging [16]. The sampler is principally a tee where a sample is collected while an FCEV is refuelled. A requirement for this strategy is of course the availability of a vehicle that is close to empty on fuel [**Error! Bookmark not defined.**] which may not be always the case. Therefore, understanding the impact of the FCEV compressed hydrogen storage system (CHSS) starting pressure level on the final hydrogen sample is important to provide guidance to the sampling operators.

It is therefore the purpose of this paper to describe the sampling procedure and purging for hydrogen sample taken at low pressure (1 to 8 MPa) and at the nozzle of hydrogen refuelling stations (dispensing at 35 or 70 MPa). This paper also investigates the air and water contamination that may be due to the sampling procedure and its implications for quality assurance of fuel cell electric vehicles. Based on the purging studies, reliable sampling procedures were tested as part of this work for oxygen, nitrogen and water concentration in hydrogen samples. Finally recommended sampling procedures for hydrogen sample taken at low pressure (1 to 8 MPa) and at the nozzle of hydrogen refuelling stations (dispensing at 35 or 70 MPa) will be presented based on the new data obtained and recommendations for future improvements will be proposed.

2. Materials and methods

2.1. Hydrogen sampling low pressure

2.1.1. Hydrogen sampling rig

The low-pressure sampling rig is a system designed to perform reliable sampling and purging for low pressure applications (i.e. hydrogen production, buffer tank). It was used for pressures below 8 MPa. The system is designed around a stainless-steel cross with a pressure gauge (G on the Figure below), a filling line with two check valves (V3 and V5) to ensure vessel sampling and another line with check valve V4 in order to purge and vent the gas before sampling. The complete system is made from Swagelok part of stainless steel 316. The sampling rig can be used with various type of cylinders from stainless steel 1-4 litres vessels to larger cylinders (i.e. aluminium cylinder 10L with double ended valves). The sampling rig was developed with a protocol to ensure proper purging of the system before the sampling is made in the vessel.

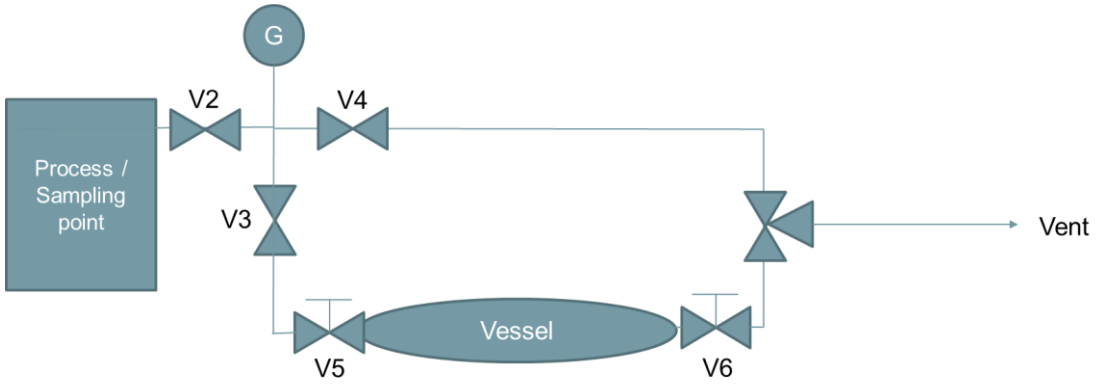

Figure 1. Schematic of the sampling system used in the project EMPIR Hydrogen 15NRM03 for hydrogen sampling from hydrogen production plant at pressure below 8 MPa.

2.1.2. Hydrogen sampling rig operation

The sampling operation involves different steps including connecting the system, purging the sampling system, sampling and disconnecting. It is mandatory to perform and agree on the safety risk assessment prior to any actual sampling.

Cylinder preparation requires that the cylinder is evacuated for at least 1 hour (1 – 2 Litres stainless steel vessel), 2 hours (4 Litres stainless steel vessel) and more than 8 hours for 10L aluminium vessel. The cylinder is evacuated to high vacuum (10^{-8} kPa). Then the sampling operation is performed in 5 steps. First the system is

connected. All the valves are in the position « Closed ». Then, the sampling system is connected to the sampling point of the process. Secondly, the system is checked for leak. Valves V2 and V3 are open and wait 15 sec (to stabilize to pressure into the sampling system). Valve V2 is then closed and the pressure on the manometer is recorded. After one minute, the pressure is checked in case of drift (indicating a leak). Then, all the valves are closed. The third step is the purge of the sampling system. The system is following cycling purges. Valves V2 and V3 are open (15 sec waiting to stabilize to pressure into the sampling system). Then the valve 2 is closed and valve V4 is opened until the manometer indicate 2 bars. Valve V4 is then closed and another cycling purge is performed. Valve V2 is opened (pressure stabilisation 15 sec waiting). Valve V2 is closed and valve V4 is opened until the manometer indicate 2 bar. The fourth step is the vessel filling (which include vessel purging). Valve V2 is opened. After 15 sec (to stabilize to pressure into the sampling system), valve V5 is opened (allowing the vessel to be filled). After 15 sec, the sampling vessel is filled and valve V5 is closed. The vessel is then purged by opening the valve V6 until the manometer indicate 2 bar. The valve V6 is closed. The vessel purging operation is repeated 7 times. Then the vessel is filled until the pressure of the system. The last step is the disconnection of the system. All the valves are closed. Then valves V2, then V3, V4 and finally vent valve are opened sequentially to depressurise the sampling system. Once the system is depressurised (check on the manometer), the vessel filled with hydrogen sample is disconnected and the sampling system is disconnected.

2.1.3. Hydrogen experiment on water removal

During the sampling campaign of the European project EMPIR 15NRM03 HYDROGEN [20], investigations were done on the number of purges required to eliminate water contamination from the hydrogen sampling rig.
The experiments were performed using a highly pure hydrogen source (PEM water electrolyser generator). The hydrogen was generated and distributed at 0.7 MPa. It was checked for oxygen, nitrogen and water amount fraction and was below µmol/mol for all the previously mentioned contaminants.
The water analyser (Quartz crystal microbalance) was implemented to monitor the amount fraction from the hydrogen generator through the path V2 – V4 and from the purging gas (V4 and V5 closed, V6 opened). The setup allowed to monitor in real time the water amount fraction during each cylinder purge to estimate the required number of purges.

The vessel used was a 1L stainless steel vessel with sulfinert® treatment (Restek, UK). The setup was implemented using the sampling rig previously described.

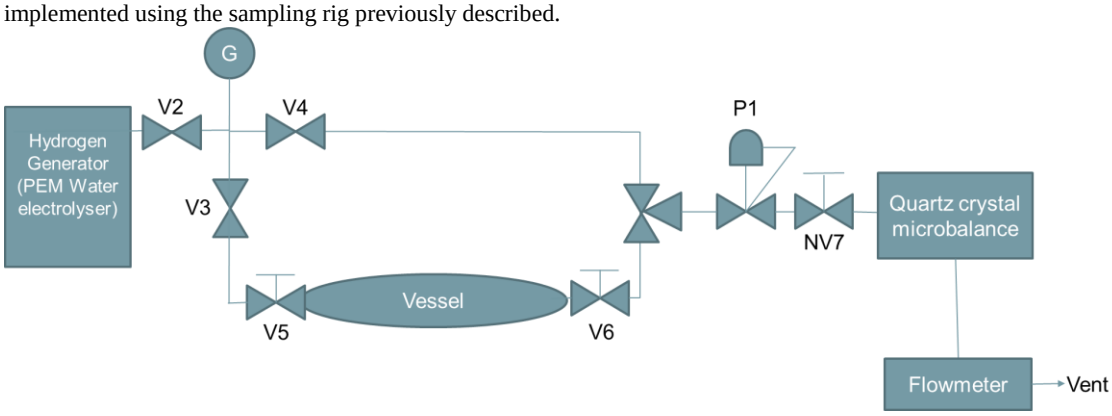

Figure 2. Schematic of the setup used to evaluate the number of purges required to eliminate all trace of water from the sampling system using the hydrogen sampling rig, an electrolyser generator at 0.7 MPa and an online analyser, quartz crystal microbalance.

2.2. Hydrogen sampling at hydrogen refuelling station (high pressure 350 and 700 bar)

2.2.1. Hydrogen sampling rig, H2 Qualitizer

The hydrogen H2 Qualitizer was used for sampling at hydrogen refuelling station. The H2 Qualitizer was developed by Linde Austria. The sampling adaptor itself is a "T-piece" inserted between a receptacle, that receives the HRS nozzle, and a nozzle, that attaches to the FCEV. The Linde H2 Qualitizer is based on a Tescom pressure regulator, located between the t-piece and the sample cylinder, with maximum pressure of 875 bar and for a temperature range of -40 to 85 °C and a maximum flow rate of 36 g/min. To prevent over-pressurisation of the sample cylinder, a pressure relief valve set at ~18 MPa is installed after the pressure regulator. The reduction valve is fitted with a DIN 477/1 connection. A high-pressure hose with quick connects is used to connect the t-piece to the Tescom reduction valve. The adaptor is not equipped with IR communication interface. The result of this is that fuelling will be limited to a lower pressure of typically~60-70 MPa, due to safety reasons (for example, no temperature feedback from vehicle hydrogen cylinders) [**Error! Bookmark not defined.**].
The system is composed of three parts [21]:

- Sample taking adapter “HG-004 adapter” to take sample during a 70 MPa hydrogen refuelling (Figure 3, number 1). The sample taking adapter has a maximum pressure of 87.5MPa, temperature range from -40°C to +85°C.
- High pressure hose including 2 DN4 quick coupling from Walther (Figure 3 number 2). The hose has a length of 2 meters and pressure rating of 100 MPa
- Pressure reducer for filling the sample taking container (Figure 3 number 3). The maximum inlet pressure is 87.5 MPa and the maximum output pressure is 16 MPa. The maximum flow rate is 36 g/min. The pressure reducer is set and sealed. A pressure relief valve is present. A safety valve is present set at 18 MPa. The pressure reducer outlet connection is compatible to 10L aluminium cylinder with spectra-seal treatment and DIN 477 N.1 valve outlet.

Figure 3. Linde H2 Qualitizer kit with numbered 1: Sample taking adapter “HG-004 adapter”; numbered 2: High pressure hose including 2 DN4 quick coupling from Walther and numbered 3: Pressure reducer for filling the sample taking container.

2.2.2. Hydrogen sampling at 35 MPa - Protocol

The H2 Qualitizer is connected to a 35 MPa nozzle (type H35). H35 dispenser is a hydrogen dispenser designed to fill vehicles that have a NWP (i.e. the Compressed Hydrogen Storage System, CHSS, pressure at 15 °C) of 35 MPa (350 bar) when the State of Charge (SOC) of the CHSS is 100%. The protocol may not be designed for all vehicles that have a receptacle that may connect to an H35 nozzle. The sample taking adapter is connected to a FCEV compatible with both 35 MPa and 70 MPa refuelling (e.g. Hyundai iX35 – however note that this will depend on the fuelling protocol employed on the dispenser).

In order to sample at the nozzle of the refuelling station at 35 MPa, it is important to follow the steps described in the H2 Qualitizer procedure from the manufacturer. The fuel cell vehicle should be compatible with the nozzle pressure required (Toyota Mirai is compatible with 70 MPa fuelling only – from the H70 nozzle).
The sampling bottle is installed and secured (using a safety belt) at the HRS location and at the suitable distance to perform the sampling. The H2 Qualitizer pressure reducer is then fixed and tightened onto the sampling cylinder valve (DIN 477 N.1) using anti-spark tools. The high-pressure hose is then connected to the pressure reducer using quick connect. Earthing and breakaway device needs to be connected to ensure safe operations. High pressure hose is then connected to the sample-taking adapter (i.e. the tee) using quick connect. Earthing and breakaway device needs to be connected to ensure safe operations. The sample-taking adapter is then attached to the FCEV receptacle. As with a standard hydrogen dispensing nozzle, the sample-taking adapter is mechanically locked on to the FCEV receptacle when properly connected. The sampling coupling is then placed on the sample-taking adapter and it get locked when properly connected. The system is then ready for sampling. It is essential to check all connections are secured and fixed.

At this step, it is possible to perform a purge of the sampling device. When the dispenser uses a nozzle that can retain pressure in the dispensing line following a fuelling, the 35 MPa nozzle is then engaged, allowing the dispensing line (if already at pressure) to pressurize the H2 Qualitizer with hydrogen from the HRS without starting any refill (If the design of dispensing nozzle/dispenser does not permit the fuelling line to remain at pressure after a fuelling, the filling protocol will need to be started, and then stopped after the initial pressure pulse – which allows the dispenser to carry out a pressure decay test). The 35 MPa nozzle is then depressurised and

disengaged. The purge valve of the H2 Qualitizer pressure reducer is slowly and carefully opened using an anti-spark tool to relieve the hydrogen in the H2 Qualitizer and purge any residual air and water from the H2 Qualitizer system.

The sampling is performed after re-engaging the 35 MPa nozzle and restarting the HRS refilling process. After the initial pressure decay test is initiated and the refill started, the valve of the 10 L sampling vessel is manually opened by the sampling operator. The valve is kept open until the FCEV refill is complete. Then the valve of the 10 L sampling vessel is closed.

The H2 Qualitizer is depressurised through the vent valve (opened slowly and carefully using an anti-sparking tool). When the H2 Qualitizer is depressurised, the sampling kit can be dismantled, and the 10 L sampling vessel is labelled according to health and safety requirement and stored in safe location.

2.2.3. Hydrogen sampling at 70 MPa - Protocol

The H2 Qualitizer is connected to a 70 MPa nozzle (type H70). H70 dispenser is a hydrogen dispenser designed to fill vehicles that have a NWP (i.e. the Compressed Hydrogen Storage System, CHSS, pressure at 15 °C) of 70 MPa (700 bar) when the SOC of the CHSS is 100%. The protocol may not be designed for all vehicles that have a receptacle that may connect to an H70 nozzle. The sample taking adapter is connected to a FCEV compatible with 70 MPa refuel (e.g. Toyota Mirai – however note that this will depend on the fuelling protocol employed on the dispenser).

In order to sample at the nozzle of the refuelling station at 70 MPa, it is important to follow the following steps process as described in H2 Qualitizer procedure from the manufacturer. The fuel cell vehicle must be compatible with the nozzle pressure required.

The sampling bottle is installed and secured (safety belt) at the HRS location and at the suitable distance to perform the sampling. The H2 Qualitizer pressure reducer is then fixed and tightened onto the sampling cylinder valve (DIN 477 N.1) using anti-spark tools. The high-pressure hose is then connected to the pressure reducer using quick connect. The high-pressure hose is then connected to the sample-taker adapter using the quick connect couplings. The earthing cable and anti-whip device needs to be connected to both the pressure regulator and sample taking adapter to ensure safe operation. The sample-taking adapter is then connected on to the FCEV receptacle. (As with a standard hydrogen dispensing nozzle, the sample-taking adapter is mechanically locked on to the FCEV receptacle when properly connected). The system is then ready for sampling. Finally, it is essential to check all connections are secure and correctly fixed.

At this step, it is possible to perform one purge. The purge is performed differently than on 35 MPa nozzle. The purge is performed by a manual stop of the FCEV refill. When the H2 Qualitizer sampling kit is ready for sampling, the sampling operator starts the refilling of the FCEV. After the HRS pressure test and when the refill starts (few grams dispensed as shown on the on the dispenser meter), the sampling operator should manually press the refill stop button. It will stop the refill while some hydrogen will be present in the H2 Qualitizer pressure reducer. To purge the system, the vent valve of the H2 Qualitizer pressure reducer is slowly and carefully opened using an anti-spark tool to vent the hydrogen in the H2 Qualitizer and purge any residual air and water from the H2 Qualitizer system.

The sampling is performed by re-initiating the HRS refilling process. After the station pressure decay test has been completed and the refill started, the valve of the 10 L sampling vessel is manually opened by the sampling operator. The valve is kept open until the FCEV refill is complete. Then the valve of the 10 L sampling vessel is closed.

The H2 Qualitizer is depressurised through the vent valve (opened slowly and carefully using anti-spark tool). When the H2 Qualitizer is depressurised, the sampling kit can be dismantled, and the 10 L sampling vessel is labelled according to health and safety requirement and stored in safe location.

2.2.4. Hydrogen sampling at various filling conditions

The objective of the study was to determine if there is an effect of purging on the final concentration of oxygen, nitrogen and water. Secondly, to investigate of the effect of the vehicle CHSS pressure prior to sampling, it was important to simulate different level of filling of FCEV.

To study different level of filling from 1/3 to 2/3 of the tank, the filling protocol was manually aborted using the stop button of the HRS. It allowed to obtain different volume of hydrogen into the sampling cylinder which was mandatory to study the impact of purging process and tank level prior to sampling.

2.3. Analytical methods

2.3.1. Gas chromatography with pulse discharge helium ionisation detector (GC-PDHID)

Nitrogen, oxygen and argon were analysed by gas chromatography (Agilent with pulsed discharge helium

ionization detector (PDHID, VICI) using helium as a carrier gas. Gases are sampled directly from the gas cylinder to the analyser, a pressure regulator (set at 20 psig outlet) and a needle valve were used to restrict the flow to 30 ml/min. The GC/PDHID sampling loop was 1 ml. The sample was then transferred onto capillary column molsieve 5A plot (30 m x 0.53 mm x 50 µm) and a second capillary column molsieve 5A plot (50 m x 0.53 mm x 50 µm). The GC oven was set at 30 degrees Celsius and the PDHID detector was set at 180 degree Celsius. NPL gravimetric gas standards in hydrogen containing nitrogen (N_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6) and oxygen (O_2) were used to calibrate the analyser. Gravimetric standards and/or dynamic standards (prepared by dilution using mass flow controller system (Bronkhorst, NL)) were used to generate calibration curve ranging from 1 to 75 µmol/mol of oxygen and 2 to 150 µmol/mol according to ISO 6145-7:2018 [22]. The method can separate argon from oxygen.

2.3.2. Quartz crystal microbalance

The measurement of water content in hydrogen sample was performed using quartz crystal microbalance, QMA401 and QMA (Michell, USA) and in few cases using cavity ring down spectroscopy (Tiger Optics, USA), for water amount fraction below 2 µmol/mol. Gases are sampled directly from the gas cylinder to the analyser, a valve was used to restrict the flow to 0.333 L/min for the QMA and to 1 L/min for the CRDS. The instruments were calibrated against primary reference standards by NPL's humidity group. Standards of water amount fraction in hydrogen were used as quality control check. The gas line was extensively purged with high purity nitrogen (BIP® quality, Air Products, BE) prior to analysis in order to remove any moisture from the tubing.

2.4. Data treatment and evaluation

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 [23]. An expanded uncertainty using a *k* value of 2 was used. In some cases, a more conservative uncertainty was derived from scientific experience.

3. Results and discussion

3.1. Low pressure sampling: purging time and water vapour amount fraction

Water is one of the most difficult contaminants to remove from a sampling rig. The most commonly method of purging is replacement of the undesired gas by either displacement or dilution. Displacement is the replacement of the undesired gas by a purge gas. Displacement is efficient in the absence of dead-end pipe which is the case of the system especially using purging through step [24].

Moreover, water tends to adsorb onto surface and can easily remain present after several purging cycles. The threshold amount fraction for water in ISO 14687-2 and EN 17124 is 5 µmol/mol which is considered low and therefore complicated to achieve during normal sampling in ambient condition (no heating, or vacuum). Ensuring that a hydrogen sample is below this amount fraction requires careful sampling and purging of the system in order to measure only the water contribution from the system and not contamination from the sampling rig which is most of the time stored at ambient conditions.

To ensure that the procedure describe in section 1.1.2 contains sufficient number of purging steps to remove all remaining water vapour from the sampling rigs and the sampling cylinder, specific setup with an online analyser was used as described in section 1.1.3.

The purging steps were tested using evacuated cylinders. The hydrogen sources used was an electrolyser providing water vapour lower that the detection limit (LoD = 1.7 µmol/mol) of the quartz crystal microbalance online analyser. The purging procedure on the low-pressure rig using evacuated cylinder showed that after 3 purges, the water vapour is completely removed from the sampling system.

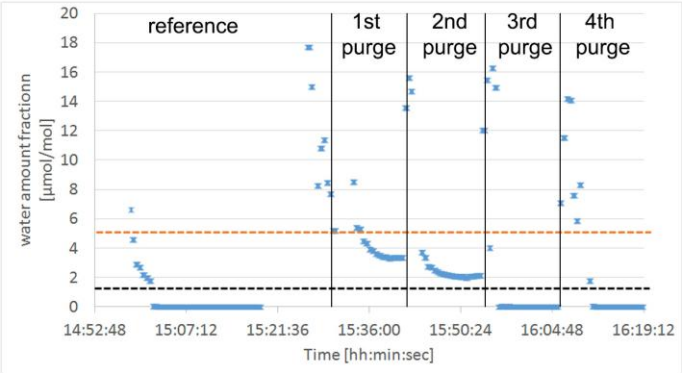

Figure 4. Water amount fraction in hydrogen at the outlet of the sampling cylinder following the low pressure sampling procedure. The black dotted line is the limit of detection of the online analyser and the orange dotted line represents the ISO 14687-2 threshold.

During the operation of sampling, the main risks are leak from sampling rig connection and potential cylinder contamination. In order to assess the impact of a leak, the sampling rig was tested with a small intended leak.
The impact of a leak in the low-pressure sampling rig was checked over several purging. Figure 5 showed clearly that the purging procedure is not capable of removing water vapour when a small leak is present in the system. It is clear that at the end of the purge, the water amount fraction increase showing ingress or diffusion of water vapour in the system from the air. The study clearly points that the sampling rig needs to be extensively leak checked prior to sampling otherwise the water vapour will be over the ISO 14687-2 threshold due to the sampling procedure. This could lead to false positives for water.

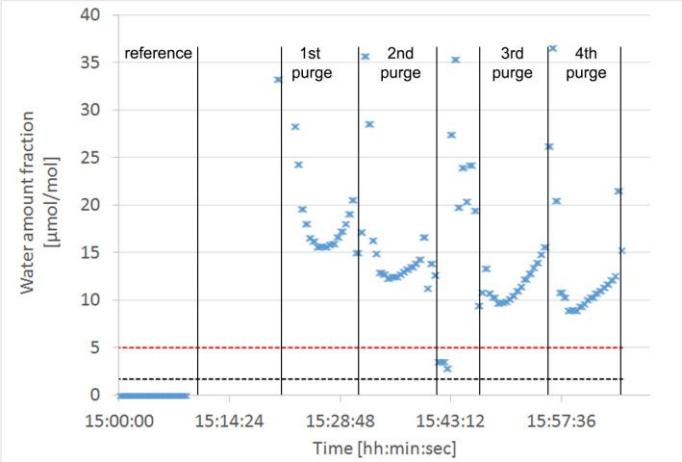

Figure 5. Water amount fraction in hydrogen at the outlet of the sampling cylinder containing a small leak following the low-pressure sampling procedure. The black dotted line is the limit of detection of the online analyser and the orange dotted line represents the ISO 14687-2 threshold.

The impact of a contaminated cylinder used for sampling was tested too. A cylinder contaminated with high level of water vapour in hydrogen ([H_2O] > 500 µmol/mol) was used to sample using the low-pressure sampling rig. The hydrogen source was electrolyser containing water amount fraction below 1.7 µmol/mol. The purging process showed clearly that the first purges were significantly reducing the water amount in the contaminated cylinder reaching a value below 1.7 µmol/mol after the 7^{th} purge. It clearly points that the purging procedure is capable of removing water vapour even from a contaminated cylinder. Even if the procedure requires that the sampling cylinder are evacuated, a small water ingress will not lead to a contaminated sample.

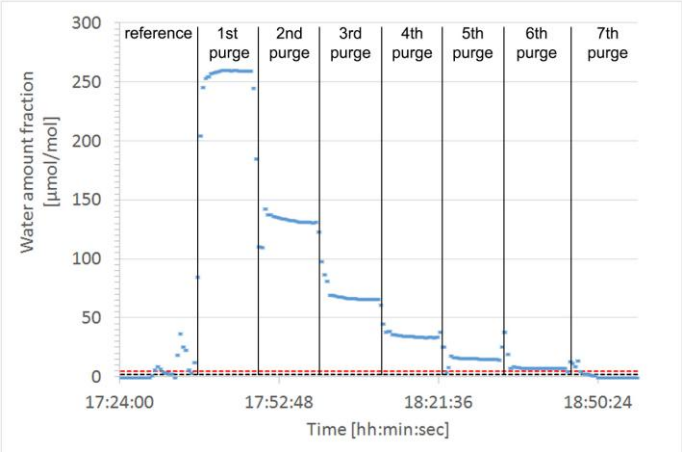

Figure 6. Water amount fraction in hydrogen at the outlet of the sampling cylinder containing a small leak following the low-pressure sampling procedure. The black dotted line is the limit of detection of the online analyser and the orange dotted line represents the ISO 14687-2 threshold.

The studies demonstrated that the low-pressure sampling rig is capable of sampling hydrogen without water contamination. The risk of having a water pre-contaminated sampling vessel was addressed and the purging procedure is capable of removing any pre-existing water contamination. The main risk is a leak from the sampling rig connection. It may lead to unacceptable water vapour amount fraction in hydrogen according to ISO 14687-2. Secondly, it is a major health and safety risk (as high-pressure hydrogen may escape producing an explosive atmosphere). Therefore, low pressure sampling rigs should be designed with minimum connection (to reduce risk of leaks) and leak testing should be done prior to sampling.

3.2. Hydrogen refuelling sampling using H2 Qualitizer

The analyses were performed according to the methods described on hydrogen refuelling stations in Europe. Two types of commercial passenger's cars were used to allow refuelling at 35 and 70 MPa. The hydrogen refuelling stations selected for this study had PEM water electrolyser feedstock. The samplings were performed on various occasions with at least two samplings per occasions. The tank level was estimated before and after filling based on the car digital gauge. The samples were analysed at NPL using NPL validated methods for water, oxygen and nitrogen amount fractions. The results are presented in the table below:

Table 1. Summary of sampling results for oxygen, nitrogen and water amount fraction in hydrogen sampled at the HRS nozzle from 35 and 70 MPa using a Linde H2 Qualitizer and purging or non-purging procedures. The FCEV tank pressure level was estimated before and after sampling, the final sample pressure and the measurement occasion was reported.

	Result of analysis Average and uncertainty (k=2) [µmol/mol]								
Sampling procedure number of purges	H_2O	O_2	N_2	N_2:O_2	HRS pressure	Approximate vehicle tank level before sampling	Approximate vehicle tank level after sampling	Final pressure in sampling gas cylinder	Day
0	3.8 ± 0.8	7.7 ± 0.3	30.8 ± 1.1	4.29 ± 0.22	70 MPa	2/3	Full	4.0 MPa	4
0	4.0 ± 0.9	9.3 ± 0.3	34.3 ± 1.1	3.68 ± 0.17	35 MPa	<1/3	1/2	5.1 MPa	4
0	1.51 ± 0.30	1.48 ± 0.10	8.4 ± 0.5	5.7 ± 0.46	70 MPa	1/2	Full	6.8 MPa	4
0	3.9 ± 0.8	6.45 ± 0.21	27.7 ± 1.0	4.29 ± 0.22	70 MPa	2/3	Full	6.9 MPa	1
0	3.7 ± 0.9	3.74 ± 0.14	18.6 ± 3.7	5.0 ± 1.1	70 MPa	1/2	Full	10.5 MPa	2
1	1.27 ± 0.30	0.5 ± 0.3	2.0 ± 0.7	4.0 ± 2.8	70 MPa	1/3	Full	7.0 MPa	4
1	3.5 ± 0.9	0.31 ± 0.10	4.45 ± 0.9	14.4 ± 5.8	35 MPa	<1/3	1/2	7.5 MPa	2
1	1.18 ± 0.24	0.27 ± 0.10	2.74 ± 0.15	10.1 ± 3.8	70 MPa	1/2	Full	9.6 MPa	1
1	3.45 ± 0.35	1.58 ± 0.10	6.10 ± 0.12	3.86 ± 0.26	70 MPa	1/2	Full	10 MPa	3

ISO 14687-2 threshold	5	5	100	

The results on oxygen, nitrogen and water amount fraction presented in Table 1 does not show correlation with the HRS pressure. No trend can differentiate hydrogen quality sampled from 35 or 70 MPa. From the estimation of vehicle tank level before and after sampling and the final pressure of the sampling gas cylinder, the relationship is not completely clear with outlier (i.e. the sixth sampling with 7 MPa pressure after almost refuelling fully the FCEV). Approximation in the tank level reading may be an explanation.

The nitrogen over oxygen ratio seems closer to an air ratio for non-purged hydrogen samples rather than for the purged samples. It should notice that in some cases the nitrogen oxygen ratio has a really high expanded uncertainty (30 – 50 %) reflecting that the oxygen or nitrogen measurement was close to the limit of detection of the analytical method.

Aarhaug et al. [25] presented hydrogen quality results from HRS sampling in Europe with only one violation of ISO 14687 threshold due to oxygen (N_2/O_2 ratio 5.96). They mentioned the possibility of air contamination for this specific sample, information on the FCEV tank emptiness would have been interested to determine if the air contamination was from the hydrogen or from the sampling procedure. No other violation was observed.

3.2.1. Impact of the purging process

Following the results of Table 1, the results of the sampling done using the H2 Qualitizer with one purge showed significantly lower amount fraction for oxygen and nitrogen compare to the sample taken without any purge. Considering air and water contamination and regarding the ISO 14687-2 threshold, the main issue of non-purging is the amount fraction of oxygen. Three out of five sampling without purge showed non-compliance on the oxygen amount fraction while all purged sampling should compliance for the same HRSs (4/4 compliant) (Figure 7).

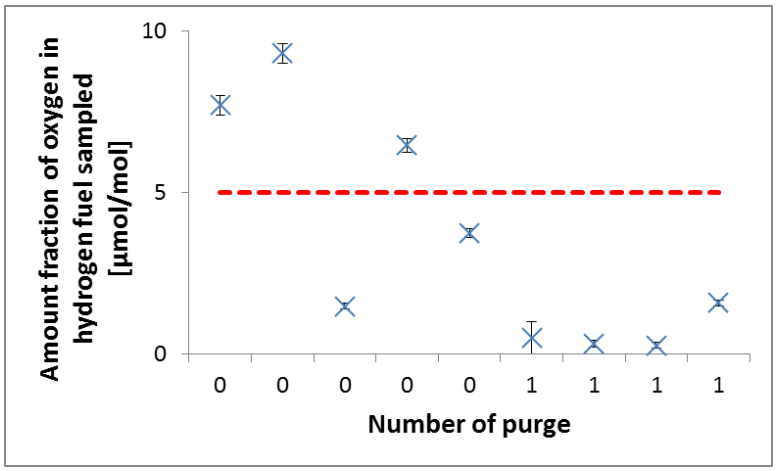

Figure 7. Results of oxygen analysis in hydrogen sampled collected using a Linde H2 Qualitizer in correlation with the number of purges performed during the sampling. The dotted line represents the ISO 14687-2 threshold value for oxygen.

However, the level of water amount fraction seems less influenced by the purge. Considering the amount fraction of water in air significantly lower than the oxygen amount fraction, the air purging will have less effect on the water amount fraction. The air purging is even more difficult as water vapour tend to be purged by displacement rather than dilution [26]. In this case the water may in dead end part of the regulators which will make difficult the displacement of water vapour. Water tend to adsorb on the steel surface [27]. As the purge is only performed once, water displacement may not be sufficient to impact significantly the results.

Aarhaug et al. [25-28] presented hydrogen quality results including oxygen, nitrogen and water amount fraction from more than 20 HRSs in Europe. The procedure mentioned that no purging of the H2 Qualitizer was performed between the sampling however they use of a FCEV with a tank almost empty according to the Linde H2 Qualitizer requirements. Few violations of hydrogen quality linked to oxygen showed possible air contamination (nitrogen / oxygen ratio). In these cases, the FCEV tank emptiness may have been a good indicator of the likelihood of false positive. On the other hand, Aarhaug et al. studies [25-28] demonstrated that adherence to Linde H2 Qualitizer requirement including the FCEV tank emptiness does not lead to a high level of false positive.

The ASTM D7606-17 [17] procedure involves purging of the sampling equipment by displacement. They recommend flowing one kilogram of hydrogen fuel gas through the high-pressure sampling system at

approximately 33.3 grams per second for a total sampling time of around 30 seconds. The H2 Qualitizer procedure studied in this article requires less gas for purging and achieve similar dehydrated level.

3.2.2. Impact of the FCEV tank level

The H2 Qualitizer is designed to perform a sampling on a FCEV with an empty tank. Therefore, the volume sampled correspond to 13.5 MPa bar in 10 L cylinder equivalent to 1350 L. The internal volume in the regulator that is not designed to be purged only represents approximately few millilitres. From the experimental results gathered on oxygen and nitrogen content on non-purged H2 Qualitizer samples, it was estimated that the non-purged volume was approximately 10 - 20 ml [21]. Considering 10 to 20 ml of air in 1350 L of hydrogen sampled means that the presence of 6 - 12 µmol / mol of nitrogen, 1.5 - 3 µmol/mol of oxygen and trace of argon will be present in all samples taken from H2 Qualitizer when the sampling of an empty FCEV is performed. It may be difficult to perform a complete refill as FCEVs are not always available with empty tank. In these cases, the amount of hydrogen sampled will be lower, for example 6 MPa, however the air contained in the unpurged section of the H2 Qualitizer remains similar (10 ml). As a consequence, the amount fraction of nitrogen and oxygen will increase significantly in the sample taken. In extreme cases, the amount fraction of oxygen due to the unpurged section of the H2 Qualitizer may reach the threshold or overcome it as observed in Table 1. The hydrogen sample may therefore be declared as not compliant with ISO 14687-2.

The use of the purge procedure described in this article removes most of the air present in the H2 Qualitizer avoiding air entering the sampling cylinder. The purge is following the dilution and displacement principles. The air is first diluted in the presence of pressurised hydrogen and then the overpressure is released reducing the amount of air in the H2 Qualitizer part 3 in Figure 1. This procedure allows sampling with an FCEV with various tank level without risking air contamination reaching a significant level in the sampling cylinder. There is no clear correlation between the FCEV tank level and the concentration of water in the hydrogen sample.

3.3. Recommendations to the hydrogen industry

The low-pressure sampling rig procedure described in this paper was proven to eliminate the risk of water contamination. A reliable sample using this method may be obtained for the analysis of “permanent gases” contaminants (e.g. Ar, He, N_2, O_2, CO, CO_2 and CH_4) and water amount fractions. The industry may implement this sampling rig including the recommendation to ensure leak tightness of the sampling rig prior to any sampling and limitation of gas connection in the field. The use of quick connect is recommended in order to avoid presence of leak during sampling which may lead to water amount fraction level above the ISO 14687-2 threshold.

Regarding HRS sampling, the Linde H2 Qualitizer with the sampling procedure proposed is suitable to obtain a reliable hydrogen sample without air or water contamination due to the sampling itself. However, the inclusion of a purging step during the sampling (where an intended release of hydrogen is carried out) may be considered a health and safety concern. Similar feedback was provided by Aarhaug [29]. While the purge is performed in a controlled way using anti-spark tools with personnel trained in handling of pressurized hydrogen gas and wearing all the safety equipment, it represents a release of hydrogen in a restricted area. Therefore, it may be required to modify the H2 Qualitizer to improve the purging system and reduce the risk of hydrogen release.

The next challenge for sampling is in obtaining reliable sample for reactive contaminants (i.e. sulphur, halogenated, ammonia or formaldehyde) as defined by Murugan et al. [30]. The nature of the sampling vessel may affect the contaminant by providing adsorption or reactive site affecting their stability prior to laboratory analysis. It is critical to determine how the sampling rig, sampling vessel and sampling procedure may affect the sampling of the reactive contaminants at low amount fraction (i.e. 100 nmol/mol of NH_3). While the procedure presented in this study is reliable for some of the contaminants listed in ISO 14687-2, the industry may support or perform the studies to verify the reliability of the sampling procedure for these reactive contaminants.

4. Conclusion

This study presents two sampling procedures achieving to remove water and air contamination from hydrogen samples taken at low (1 – 8 MPa) and high (35 & 70 MPa) pressures. For low pressure sampling (i.e. hydrogen production or HRS buffer tank), the purging protocol demonstrates that water contamination is completely removed after 7 purges even from a contaminated sampling vessel. For sampling from 35 and 70 MPa hydrogen dispensing systems, the Linde H2 Qualitizer provides a hydrogen fuel sample following the refill protocol and complies with ISO 19880-1 in term of utilizing hydrogen from all hydrogen banks at fuelling stations. Regarding the operating procedure, the non-purging protocol is acceptable for a sampling during the refuelling of an empty to half empty FCEV tank. Considering FCEV tanks with more than half empty, the H2 Qualitizer purge is needed to avoid false positives (contamination from the sampling procedure, especially for oxygen with ISO 14687-2 threshold of 5 µmol/mol). Based on the study, it may be recommended to perform a purge when using the H2 Qualitizer in any case and to consider parameters like the FCEV level of emptiness during the hydrogen quality sampling. The drawback of this approach is the health and safety issues of releasing hydrogen into the local

atmosphere twice rather than once (at the end of sampling). The H2 Qualitizer may therefore need a design update ideally with consultation of HRS operators to understand how to improve the sampling procedure from an ATEX perspective.

Several pitfalls and common issues presented in this study need to be addressed prior to hydrogen sampling at HRS (procedure not validated, lack of leak checking, and insufficient purging). The study demonstrated that a non-properly tested and validated procedure may lead to false results and false positive (oxygen or water above 5 µmol/mol). The impact of such false positive may be HRS operation stopped and investigation on hydrogen quality. The cost of it may be significant and this study provide validated procedure for sampling at production side (i.e. hydrogen production such as steam methane reforming or electrolyser) and at the nozzle of the HRS using the H2 Qualitizer.

The study highlights the requirement to standardise hydrogen sampling for FCEV application at the HRS nozzle with clear guidance on the critical parameters as the ones highlighted in this study. The next challenge is to demonstrate that reliable sampling is achieved for reactive contaminants (i.e. sulphur, halogenated, ammonia or formaldehyde). The nature of the sampling vessel may affect the contaminant by providing adsorption or reactive site affecting their stability prior to laboratory analysis. It is currently unclear how the sampling system may affect the amount fraction of such reactive contaminants in the hydrogen.

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