METROLOGY for HYDROGEN VEHICLES

GOOD PRACTICE GUIDE:

Good Practice Guide on effective sampling and transportation of hydrogen from the refuelling station as required by ISO14687

This good practice guide was written as part of activity A4.1.7 from the EMPIR Metrology for Hydrogen Vehicles (MetroHyVe) project. The three- year European project commenced on 1st June 2017 and focused on providing solutions to four measurement challenges faced by the hydrogen industry (flow metering, quality assurance, quality control and sampling). For more details about this project please visit www.metrohyve.eu.

This report was written by:

Karine Arrhenius	RISE	*Karine.arrhenius@ri.se*
Oliver Büker	RISE	*Oliver.buker@ri.se*
Sam Bartlett	NPL	*Sam.bartlett@npl.co.uk*
Thor Aarhaug	SINTEF	*Thor.a.aarhaug@sintef.no*
Darío Cortés	FHa	*dcortes@hidrogenaragon.org*

This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union’s Horizon 2020 research and innovation programme.

Contents

1 - Introduction

The issue of correct sampling is a common topic among the hydrogen industry. It is crucial to sample a volume of hydrogen that is fully representative of the fuel dispensed at the station. There are 4 steps when taking a sample:

1) Preparation of the vessels before the sampling: the vessel must be totally free from impurities
2) Transportation of the vessels to the sampling site
3) Sampling; including necessary purge of the sampling device
4) Transportation of the sample to the analysis laboratory; the composition of the sample shall remain stable between the time of the sampling and the analysis

Erroneous results can arise from using an inappropriate sampling approach during each of the above-mentioned steps. There are two scenarios where false results (negative or positive) could occur due to poor sampling.

A false positive (over-estimation) would be the case where the hydrogen is sufficiently pure but the sampling procedure itself contaminated the sample. Examples of this would be an air leak in the system allowing ingress of oxygen and nitrogen into the hydrogen sample or presence of contaminants in the vessels before sampling.

A false negative (under-estimation) would be the case where impurities in the hydrogen are lost either during the sampling or transport of the gas sample vessel. An example of this could be hydrogen sulphide which may adsorb to stainless steel walls (such as in the sampling device or sampling vessel) and therefore would be lost or significantly reduced in the sample upon reaching the laboratory.

In this report, we focus on the most likely sources of contamination; air and water.

The ISO 14687-2 [1] levels of oxygen, nitrogen and water respectively are, 5 $\mu mol.mol^{-1}$, 100 $\mu mol.mol^{-1}$ and 5 $\mu mol.mol^{-1}$. Therefore, even a small ingress of air or moisture is likely to affect the purity.

In this report, we describe two procedures that have been developed and tested during the project MetroHyVe to eliminate the risk of contamination of air and water.

- Procedure(s) for preparing vessels at the laboratory before sampling
- Procedure to purge the sampling device at the HRS including a discussion on the number of purges that are required

2 - Considerations

To avoid false positives for air and moisture a rigorous evacuation or purging cycle must be performed. There is currently no standard procedure for the preparation of sample cylinders for hydrogen fuel quality control even if purging procedures are mentioned in ASTM D7606-11 [2] and ISO19880-1 [3].

Oxygen and nitrogen are not as adsorptive to stainless steel compared to water, so a good number of purges should be enough to remove any perceived contamination, however it should be noted that it does entirely depend on the sampling device set-up as any dead volumes or dead ends may simply end up compressing and decompressing the pocket of air without actually removing it from the system. Air contamination could occur through ingress of air into the sampling vessel during transport (more likely during transport of evacuated vessel to the station). In addition to this ingress affecting the quality of measurements, it could lead to a hazardous scenario where hydrogen may directly blend with oxidising agent. To minimize this risk, the time between evacuating the sample vessel and taking the sample must be as short as possible.

3 – Evacuation procedures currently in use in standards

Both standards (ASTM D7606-11 and ISO19880-1) propose specific purging procedures of the HQSA (Hydrogen sampling quality apparatus).

It is specified in ASTM D7606-11 that the HQSA and the cylinder are to be cleaned by pressurizing and releasing hydrogen from the HQSA and the sampling cylinder at least 10 times (6.7) to ensure a valid sample. This procedure (9.2) should be performed at a specific flow rate (33.3 g/s) as at this flow rate the targeted impurities will be removed from within the HSQA and sampling lines (dehydrating and removing residual sulphur gases from the HSQA, the sampling line and the sampling cylinder).

In ISO19880-1, if purging is needed, sampling shall be initiated but aborted by pressing the Stop button on the dispenser within 15 seconds in order to isolate the test pulse. The sampling device is then depressurized using a bleed valve. Another option for purging is to perform the procedure without connecting the HQSA to the vehicle. In that case, the safety at HRS will automatically shut off the refuelling of hydrogen.

In standard ASTM D7606-11 (10.4), it is specified that two to three sample cylinders shall be taken for a hydrogen sample at a HRS since the analyses of two sampling cylinders for each sample may be necessary to prove the existence and validate the amount of a contaminant in a hydrogen fuel system.

4 – Sampling procedure

In this report, we focus on the sampling procedure “parallel sampling using the Linde Qualitizer”. The sampling is performed while refuelling a car.

An adaptor (a tee) is inserted between the HRS nozzle and the vehicle (Figure 1).

Figure 1: Installation of the Linde Qualitizer

The adaptor is connected to a reduction valve rated for 1000 bar through a high-pressure hose with quick connects. Electrical grounding is provided for both quick connects. The maximum pressure after the reduction valve is 160 bar. The reduction valve is connected to a sampling cylinder (typically 10 litre). As the adaptor is not equipped with a communication interface, there will be not feedback on temperature and pressure sent from the vehicle and the refuelling will be slower. Fast filling of the sample cylinder is prevented using a throttle valve (the filling takes approximately 3 minutes).

The installation is done from the cylinder and back to the HRS nozzle. The refuelling sequence is started; the cylinder is slowly filled. Then the cylinder valve is closed. The sampling line is depressurized by slowly opening the vent valve.

A picture taken during sampling is presented on Figure 2:

Figure 2: Sampling in 10-litre cylinders using Linde Qualitizer

5 – Evacuation methods developed during MetroHyVe and HyCoRa

5.1- Purging cycles

The procedure for purging adapted in the HyCoRA project has been to evacuate 10 L, spectra-seal cylinders to 1 mbar, followed by pressurization to 10 bar with UHP (Ultra High Purity) hydrogen. This procedure was repeated three times before the cylinders were finally evacuated to 1 mbar prior to sampling use. The method was established as a compromise for single-ended cylinders, where purge-through (ASTM D7606-11) could not be applied. The choice of pressure levels and repeat cycles was chosen arbitrarily and has not been evaluated with respect to performance.

5.2 - Turbo evacuation

This section summarises NPL's procedure for preparing a sampling vessel. It requires use of a roughing pump whose function is to evacuate the initial content of the sampling vessel, a turbo pump whose function is to evacuate the trace content of the sampling vessel by achieving a high vacuum and residual gas analysis whose function is to monitor outgassing of air, moisture and any remaining contaminants. These combined components are called the 'evacuation rig' (Figure 3).

Figure 3: NPL's evacuation rig in operation

The procedure includes the following steps:

1. Prior to attaching a cylinder to the evacuation rig, blow down the cylinder in a fume cupboard or extraction vent until empty, then close the cylinder valve when at atmospheric pressure.
2. Connect cylinder to evacuation rig using an appropriate cylinder valve connector.
3. If other cylinders are already on the evacuation rig, the cylinder valves of each of them must be closed before starting the evacuation of any additional cylinders.
4. Use the roughing pump to partially evacuate the cylinder prior to opening the turbo pump.
5. Once the pressure in the vessel is at around 1.1 x 10^{-1} mbar or less, activate the turbo pump.
6. Once at a suitable vacuum turn on the residual gas analyser to monitor outgassing of air, moisture and any remaining contaminants.
7. Allow cylinder vacuum to reach 1 x 10^{-7} mbar.
8. Monitor impurities on the residual gas analyser (Figure 4), if an expected impurity remains within the system this should be removed by heating or including a subsequent hydrogen purge step.

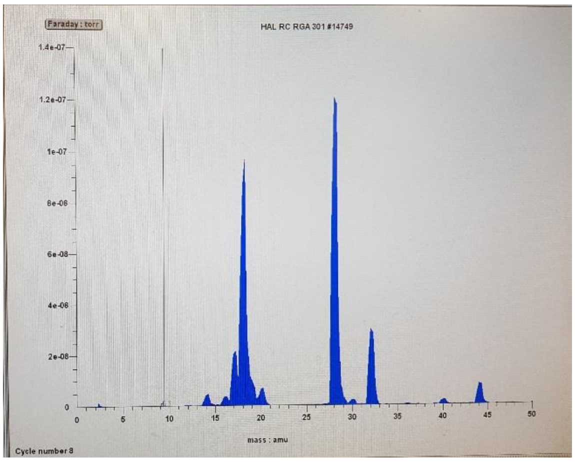

Figure 4: Mass spectrometer data from residual gas analyser indicating negligible levels of air and moisture

9. Close cylinder valve and remove from evacuation rig.

6 – Verification of the suitability of the evacuation methods

6.1 – Suitability of the "purging cycles" method

The SINTEF approach has not been validated at the laboratory but has been evaluated to be sufficient for some compounds based on a campaign of 40 samplings performed at HRSs where no evidence from carry-over from one sample to the next has been observed.

It should be noted that for these samples only a few serious violations of the hydrogen purity standard (ISO 14687-2) were observed, and more rigorous cleaning of the cylinders could be required in the case of more serious violations. In the case of a violation of fuel quality it was investigated if there was any carry-over to the next sample.

Table 1 shows two cylinders that were used for sampling where fuel quality was not in compliance with ISO 14687-2. From the contamination observed it appears that the applied method of purge and evacuate works for the observed impurities (N_2, CO_2, O_2, CH_4). No conclusion can be drawn for other species as those have not been found in any samples, no evaluation of eventual carry-over could be made.

Table 1. Sampling results with fuel tolerance violations.

	Cylinder 1		Cylinder 2	
	Sampling 1	Sampling 2	Sampling 1	Sampling 2

Fuel Index (%)	99.8551	99.99371	99.95574	99.999
H2O	2.9	ND	ND	ND
THC (C1)	0.55	0.36	5.1	1.7
O2	4.1	5.7	13	ND
N2/AR	1444	18	419	8
CO2	0.43	ND	5.7	ND
TS	0.00040	0.00003	0.00011	0.00001
C4Cl4F6	0.019	0.00048	0.001	0.0026

ND: non detected

6.2 – Suitability of the "turbo evacuation" method

The NPL turbo evacuation method has been validated by preparing a 10-litre cylinder using the procedure outlined in Section 5.2. The evacuated cylinder was then filled with high purity, dry hydrogen to approximately 100 bar pressure. The residual water concentration within the 10-litre cylinder was then measured by cavity ring-down spectroscopy, following a purge with high purity, dry nitrogen. See Figure 5 for results.

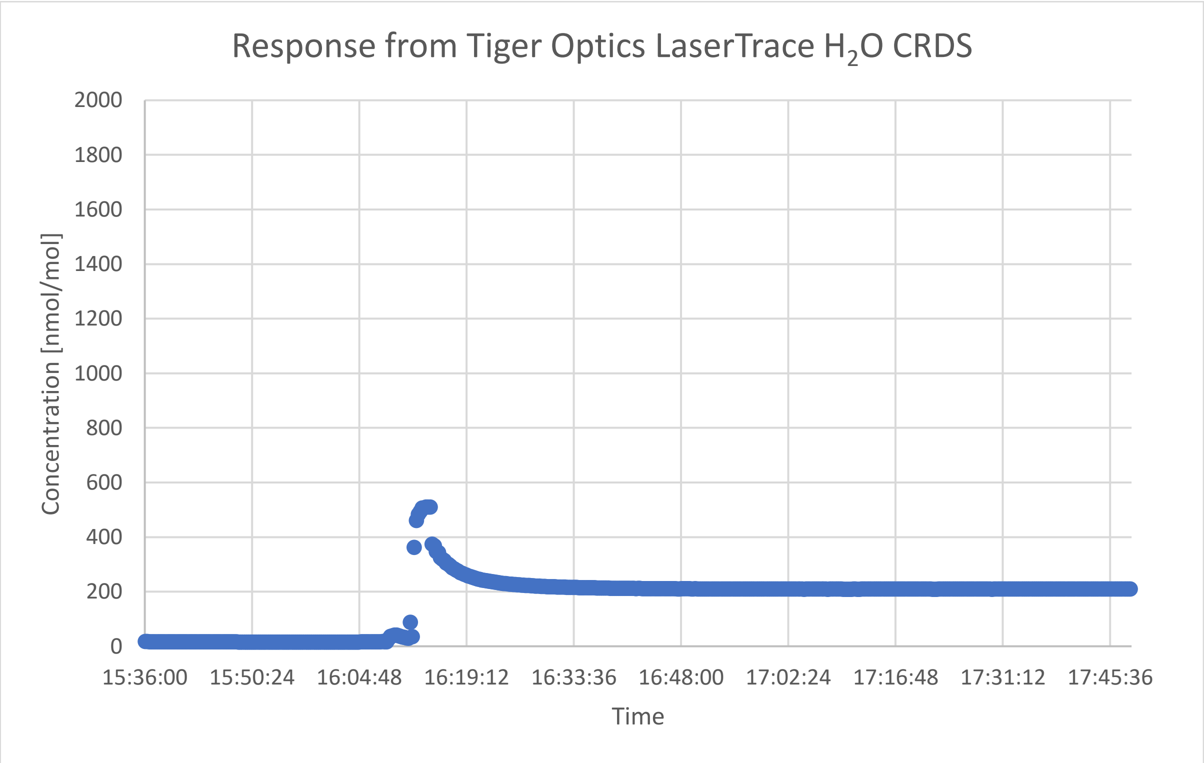

Figure 5: Output from H_2O CRDS analyser whilst a cylinder containing dry hydrogen is passing through.

Analyser indicates that approximately 200 nmol/mol Water remains in the cylinder/hydrogen following the Turbo Evacuation procedure.

Water is a likely contaminant in sampling devices as it is fairly difficult to remove through purging. It is a good idea to ensure that sampling devices are closed off, for example using a gas valve, when not in use to avoid entry of ambient air over time. Residual moisture can be removed from the system though high-pressure cyclic purging (either using refuelling station hydrogen or a separate feed of high-pressure inert gas).

The water amount fraction in the vessel is highly dependent on the sampling system. It is crucial to adapt the sampling system purge to the pressure of the process or HRS (low or high pressure). Secondly ensuring purging of the system before taking the sample will avoid contamination from ambient humidity: sampling under the rain, or in dry summer. Ensuring that all parts of the sampling device are leak tight will reduce the number of purges required.

6 – Procedure to purge the sampling device at the HRS

6.1 – Pre-filled cylinder purging

This approach uses 10 litre cylinders that have been pre-filled with UHP hydrogen to a pressure of 2 bar. This slight over-pressure of UHP hydrogen is then used to purge the sampling apparatus (specifically the Linde Qualitizer) to remove residual air present within the dead volume between the sampling apparatus and the sampling cylinder.

Storage and transport of pre-filled cylinders containing gas at above atmospheric pressure means that air and moisture ingress into the cylinders is minimised as it is more likely that hydrogen from the cylinder would egress, if at all. Therefore, pre-filled cylinders can be stored safely for a longer period than evacuated sampling cylinders without risk of contamination. It is also safer to undertake purging of the sampling apparatus using gas at a low pressure, resulting in a relatively small volume of hydrogen being released on-site at the HRS.

The presence of the 2 bar UHP hydrogen within the pre-filled 10-litre cylinders will have an impact upon the sample obtained at the HRS in that the gas sample will be diluted. The degree of dilution will vary depending upon the volume of gas sampled form the HRS, however the impact of the dilution is quite low. When undertaking analysis of impurities within the sampled obtained using this method, a correction needs to be applied to account for the sample dilution from the UHP hydrogen. This correction will have the effect of increasing the measured impurity concentrations to account for the dilution and provides more representative quality information of the hydrogen sampled. The correction required can be calculated using the equation below:

$$CF = \frac{(V_c P_1) - (V_p n)}{(V_c P_2)}$$

Where CF is the correction factor to be applied to measured impurity concentrations, V_c is the cylinder volume, P_1 is the pre-filled cylinder pressure, V_p is the sampling apparatus dead volume, n is the number of purges and P_2 is the cylinder pressure after sampling.

Pre-filled 10-litre cylinders can be purchased directly from commercial gas suppliers. Alternatively, the procedure for preparing pre-filled 10-litre cylinders can be found below in Section 6.2.

6.2 – Cylinder preparation

Cylinders are first evacuated using the procedure outlined in section 4.2 of this report.

1. Following evacuation, a 10-litre cylinder is placed on a weighing balance and connected to a cylinder of UHP hydrogen using a pressure regulator and appropriate transfer line.
2. The pressure regulator and transfer line are then evacuated or purged prior to transfer of UHP hydrogen.
3. Open the valve of the UHP hydrogen cylinder and use the pressure regulator to pressurise the transfer line to approximately 5 bar.
4. Tare the weighing balance.
5. Open the valve of the 10-litre cylinder to allow flow of UHP hydrogen to commence.
6. Fill 10-litre cylinder with 1.65 g of UHP hydrogen and close both cylinder valves.
7. Disconnect transfer line and pressure regulator safely, making sure to safely vent residual UHP hydrogen.
8. Remove 10-litre cylinder from weighing balance and store appropriately until required for sampling.

6.3 – Verification of the method's suitability

The pre-filled cylinder purging method has been validated by preparing three 10-litre cylinders using the procedure outlined in Section 6.2. Samples were then obtained from a HRS using the Linde Qualitizer and using the UHP hydrogen within the three pre-filled 10-litre cylinders to purge the sampling apparatus 0, 1 and 5 times. The concentrations of oxygen, nitrogen and water within the hydrogen samples were then quantified using a gas chromatograph coupled with pulsed helium discharge ionization detection and a quartz crystal microbalance analyser. See Table 2 for results.

Table 2. Results from pre-filled cylinder purging method validation

Number of purges	Oxygen amount fraction (µmol mol^{-1})	Nitrogen amount fraction (µmol mol^{-1})	Water amount fraction (µmol mol^{-1})
0	5.99 ± 0.38	24.0 ± 1.5	2.04 ± 0.12
1	1.08 ± 0.07	6.31 ± 0.35	1.15 ± 0.07
5	0.57 ± 0.06	4.41 ± 0.27	0.494 ± 0.042

The ISO 14687-2 [1] levels of oxygen nitrogen and water respectively are, 5 µmol.mol^{-1}, 100 µmol.mol^{-1} and 5 µmol.mol^{-1}. Purging 1 time reduces the ingress of oxygen and water to around five times less than the ISO14687-2 levels. Additional purging (here 5 times) reduces the ingress with an additional factor of 2.

7 - Transportation

The transport conditions must guarantee the integrity and characteristics of the samples. From completion of sample collection to laboratory analysis, every effort should be made to:

- Avoid contamination of the sample

- Minimise any changes to the sample

To maintain the integrity of the samples, procedures for collection, transport, storage conditions, final destination and security, as well as adequate supervision, should be designed. The control of all these conditions will bring added value to the samples, as it will guarantee their quality and traceability. Hydrogen is legally classified as dangerous to transport by the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR), in the International Regulations Concerning the Carriage of Dangerous Goods by Rail (RID), International Maritime Dangerous Goods (IMDG) and the International Air Transport Association (IATA). The hazards associated with the handling of hydrogen are fire, explosion and pressure, so the transport of the sample must be based on existing legislation to avoid and prevent risk and exposures.

The container shall be appropriately marked in accordance with the regulations in force. The markings on labels must be clearly legible and permanent in order to prevent deletion or substitution/alteration during storage, handling and transport.

The hydrogen UN number is 1049 and its United Nations Transport Officer Designation is "HYDROGEN COMPRESSED". The transportation hazard Class is class 2 and the label must be 2.1 (flammable gas) and GHS 04 (compressed gas).

Figure 1. Label 2.1 (left) and GHS 04 (right).

The following section shows a brief summary of the specific legislation on the transport of hydrogen in each mode of transport. For further information it is recommended to refer to the legislation.

Road transport

The legislation on road transport is included in the ADR. Hydrogen is listed in the table a, list of dangerous goods in numerical order by UN number, in the chapter 3.2.

The permitted vessels are defined in these regulations, as well as the rules about loading and unloading and handling:

- Vessels should not be thrown or stuck.
- Containers should be stowed in vehicles or containers so that they cannot overturn or fall.
- Cylinders with a capacity of not more than 150 L shall be lying in the longitudinal or transverse direction of the vehicle or container.

- Cylinders close to the transverse wall at the front should be placed in a transverse direction.
- Cylinders of short and large diameter (about 30 cm or more) can be placed longitudinally, with the valve protection devices oriented towards the centre of the vehicle or container.
- Cylinders which are sufficiently stable or which are transported in suitable rollover protection devices may be placed in a vertical position.
- Lying cylinders shall be shimmed, restrained or secured securely and appropriately so that they cannot be moved.

Packages should preferably be loaded in uncovered or ventilated vehicles or in open or ventilated containers. If this is not possible and the packages are loaded onto other covered vehicles or closed containers, the loading doors of these vehicles or containers should be marked as follows, with a font size of at least 25 mm. high: "ATTENTION WITHOUT VENTILATION OPENING WITH CARE". This should be written in a language that the consignor deems appropriate.

There are no general legal requirements for vehicles carrying hydrogen to use specific roads or follow prescribed routes. Certain road restrictions may be imposed at national or local level by the competent authorities. e.g. for avoiding residential areas.

The tunnel restrictions do not apply for carriage of small quantities of compressed hydrogen (up to 333 L) per transport units in packages, when carrying only hydrogen on board, and there is no need of having warning plates indicating that dangerous good are being transported. Parking restrictions apply for compressed hydrogen when the total mass or volume in the vehicle exceeds 10 000 kg as packaged goods or 3 000 L in tanks.

Rail transport

The RID contains regulations on the transport of dangerous goods by rail as in the ADR. Hydrogen (UN 1049) is listed in table a, chapter 3.2. At this point all regulations for this are listed, including regulations that must be complied with by the tanks and packaging general instructions. It is established that it may be transported in packaging combined with other goods of Class 2; with goods of other classes, where common packaging is also authorised for them; or with goods which are not subject to the provisions of the RID, provided that they do not react dangerously between them.

It also contains provisions on loading and unloading and handling similar to the ADR recommendations, but referring to wagon or containers.

Maritime transport

Compressed hydrogen is listed in the IMGD Chapter 3.2. The IMGD, International Maritime Dangerous Goods, establishes the regulations that the tanks must comply with, as well as the periodic controls that they must be subjected to. In addition, general packing instructions are established.

Air transport

The IATA Dangerous Goods List Compressed includes compressed hydrogen (table 3.1). According to the air transport system, the regulations establish a special provision according to the packaging, in which the permitted bottles are detailed. The transport in passenger airplanes is prohibited, it is only allowed in cargo aircraft with a maximum net quantity per package of 150 kg.

There are some state discrepancies in these regulations listed in Attachment 3. The countries presenting it are Australia, Canada, Great Britain, Iran, the Netherlands and the United States.

Marking and documents accompanying final samples

Each sample must be individually coded. This coding shall allow the traceability of the sample during the transport, storage and analysis process.

All essential information for the laboratory will be indicated on a label on the containers. These labels shall be securely affixed to the sample containers, but shall not hinder their use. The information given shall preferably include:

- The number of the container;
- The type of container;
- The place where the sample was taken;
- All the information necessary for the identification of the sampled carcase;
- The date and time; or the period of sampling;
- Sample procedure;
- The actual destination of the container;
- Any maintenance required on the container (e.g. leaks);
- Any useful information for the analytical laboratory concerning the sample;
- The pressure of the sample, if the vessel does not incorporate a manometer;
- The pressure in the reservoir;

Copies of other relevant documents relating to the nature of the sample (safety data sheets, technical specifications, etc.) and the ADR Transport document (delivery note) or similar may be attached.

Samples handling

After sampling, the vessels may be checked for leaks. If leaks occur, the lids should be reinforced. If leaks persist, a new sample should be taken in a new vessel and the procedure for detecting leaks should be restarted.

The vessels should be protected from physical damage; do not drag, slide, roll or pull. When the vessels are moving, even over short distances, a cart designed to transport these containers are required.

Sample vessels containing pressurised gas shall be transported in accordance with the applicable regulations. Constant pressure vessels should always be protected in containers. Otherwise, containers and/or valves, probes, etc. may be damaged. During transport, the containers must also be protected against certain temperature conditions which could cause overpressure or condensation on the sample.

Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking. Use only non-sparking tools. Use only explosion-proof equipment. Wear leather safety gloves and safety shoes when handling cylinders.

Storage of samples

Storage conditions should ensure that the sample is not altered in any way that could affect the parameters to be analysed. Health and safety regulations must be observed.

All electrical equipment in storage areas must be compatible with the risk of potentially explosive atmospheres. Separate from oxidizing gases and other oxidizing materials during storage. Containers should not be stored in conditions that may favour corrosion of the container. Containers should be checked periodically to ensure proper conditions of use and no leaks. The valve protections must be in place. Store containers in places free of fire risk and away from sources of heat and ignition. Keep away from combustible materials.

8 – Conclusion and Future work

In order to sample a volume of hydrogen that is fully representative of the fuel dispensed at the station, every step from the vessel preparation to the transportation must be undertaken following procedures that have been validated. In this report, we focused on the most likely sources of contamination while sampling; air and water. Discussions about cylinder suitability for other impurities are dealt with in other parts of the MetroHyVe project such as task 4.4 (assessing suitability of commercially available sampling vessels).

This practice guide presents two evacuation procedures to prepare cylinders before sampling; a method using purging cycles and a method using turbo evacuation.

Moreover, in the guide, we present a method to pre-fill the cylinder with UHP hydrogen which presents two advantages: 1) air and moisture ingress into the cylinders is minimised as it is more likely that hydrogen from the cylinder would egress; consequently pre-filled cylinders can be stored safely for a longer period than evacuated sampling cylinders and 2) the hydrogen in the cylinder is used to remove residual air present within the dead volume between the sampling apparatus and the sampling cylinder.

All the methods validated here are for the combination 10-litre cylinder and Linde Qualitizer. The same validation approach should be undertaken if other sampling vessels or sampling device are to be used.

9 - References

[1] ISO14687-2:2012: Hydrogen fuel – product specification – part 2: proton exchange membrane (PEM) fuel cell applications for road vehicles

[2] ASTM D7606:1 including Annex 1, Sampling procedures and Hardware for Hydrogen Fuel Quality Analysis

[3] ISO/TS 19880-1:2016: Gaseous hydrogen – Fuelling stations . Part 1: General requirements

[4] 2010/35/EU Directive on transportable pressure equipment and repealing council directives 76/767/EEC, 84/525/EEC, 84/526/EEC, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex:32010L0035