

METROLOGY *for* HYDROGEN VEHICLES

REPORT:

A4.1.1 Sampling from hydrogen refuelling stations

This report was written as part of activity A4.1.1 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.

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The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Contents

1 - Introduction.....	3
2 - Overview of a hydrogen refuelling station.....	3
3 - Standards.....	3
4 - Sampling locations	4
5 - Sampling methods.....	4
5.1 - Parallel sampling:	4
5.2 - Series sampling.....	5
5.3 - Available sampling devices.....	7
5.4 - Available sampling vessels	8
6- Risk assessment sampling	8
6.1 – False positives (over-estimation).....	9
6.1.1– Air leaks	9
6.1.2 – Water	9
6.1.3 – Carry-over	9
6.1.4 – Cleaning/purging	10
6.2 – False negatives (under-estimation)	10
6.2.1 – Loss due to adsorption	10
6.2.2 - Reactions	10
7 – Current recommendations	11
8 – Future work	11
9 - References.....	13

1 - Introduction

There are two common methods to control the quality of hydrogen at a Hydrogen Refueling Station (HRS), by so called spot sampling or by continuous monitoring. Continuous monitoring or online sampling, discussed in WP3 (Hydrogen Quality Control) of this project will not be addressed here.

Spot sampling at a HRS involves drawing a sample of gas that is subsequently sent to a laboratory for analysis. It requires specialized sampling equipment and personnel to operate it. The advantage of spot sampling [1] is that a more detailed laboratory analysis can be performed on the sample using a large range of analytical instruments. The disadvantages are that results are not obtained directly on-site and are representative of a single point in time. Moreover the equipment needed for the sampling including sampling line and vessels could change the composition of the sample (through loss or gain of some compounds by, for example, adsorption of compounds to metal surfaces or ingress of air through leaks).

In this report, an assessment of the possible causes for contamination and other issues that would arise from a poorly performed sampling of hydrogen at the HRS will be studied. The focus is on the sampling for the analysis of gaseous compounds i.e. not the particulates. The report also includes an overview of the sampling devices and sampling vessels that are currently available.

2 - Overview of a hydrogen refuelling station

At a hydrogen refuelling station, hydrogen is compressed to about 350-700 bars pressure on site and is then dispensed into the vehicle via a dispenser similar to the ones used in petrol stations [2].

Hydrogen arrives at a filling station on a truck but can also be generated on-site. Hydrogen can also be transported via pipes. If hydrogen arrives in liquid form, it must first be converted into a gas before it can be used. Low pressure hydrogen is stored in bottles (cylinder racks), tanks or tube trailers above ground. Any leak in a storage tank means that hydrogen, which is lighter than air, simply vents away before it has the chance to combust.

Before hydrogen goes into a car, it must be compressed to high pressures up to 700 bar. There are two standard pressures for hydrogen compression: half-pressure H35 and full-pressure H70. Once the pressure has been increased (350 or 700 bar), hydrogen is stored in buffer tanks. As hydrogen is compressed into a vehicle tank, it heats up. The vehicle tanks are nearly all made of carbon fiber and have thermal limits that must not be exceeded. To prevent expansion and to maintain energy density while being pumped in at high pressures, hydrogen is cooled as low as -40°C using the exchanger and the refrigeration unit. Finally, the hydrogen goes to the pump which has the ability to communicate with the fuel-cell vehicle's onboard computer, it can determine temperature, tank pressure and fuel levels. Hydrogen is refuelled within a few minutes.

3 - Standards

There are currently two standards for sampling at a HRS:

- ISO19880-1, annex I; sampling procedures and hardware for hydrogen fuel quality analysis which is under revision in working group 24 of the technical Committee TC 197 (Hydrogen Technologies)
- ASTM D7606:1, Standard Practice for Sampling of High Pressure hydrogen and related fuel cell feed gases

Different methodologies exist for sampling hydrogen to analyse the gaseous impurities. These methodologies are described in detail in the standards.

4 - Sampling locations

Three possible locations for the sampling have been identified during the workshop “Hydrogen Contamination Detector” organized in June 2014 [2,3]:

- Immediately downstream of the gas source: the results of the analysis will allow identifying any impurities due to the production method. The pressure here is often quite low.
- Immediately upstream at the fueling nozzle: Sampling here would capture contaminants from all system components except the dispenser piping, hose and fueling nozzle. The big advantage of sampling here is that at other locations, station configurations vary. However, if poor quality fuel is analyzed here, it would require further investigation by the station operator as any of the upstream components may be responsible.
Pressure: up to 900 bar
Temperature: can be -40°C under normal conditions
- In between some system components: the temperature requirement could be relaxed if sampling is performed between upstream station components. In general, two choices exist: before the chiller and after the compressor.

5 - Sampling methods

5.1 - Parallel sampling:

For parallel sampling, the sampling operation is performed whilst refuelling a car.

Description of the sampling procedure and equipment (HQSA: Hydrogen sampling quality apparatus):

An adaptor, a tee (Figure 1) is inserted between the HRS nozzle and the vehicle. 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 1-10 litres). 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 refueling 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.



Figure 1: Tee adaptor used in parallel sampling

5.2 - Series sampling

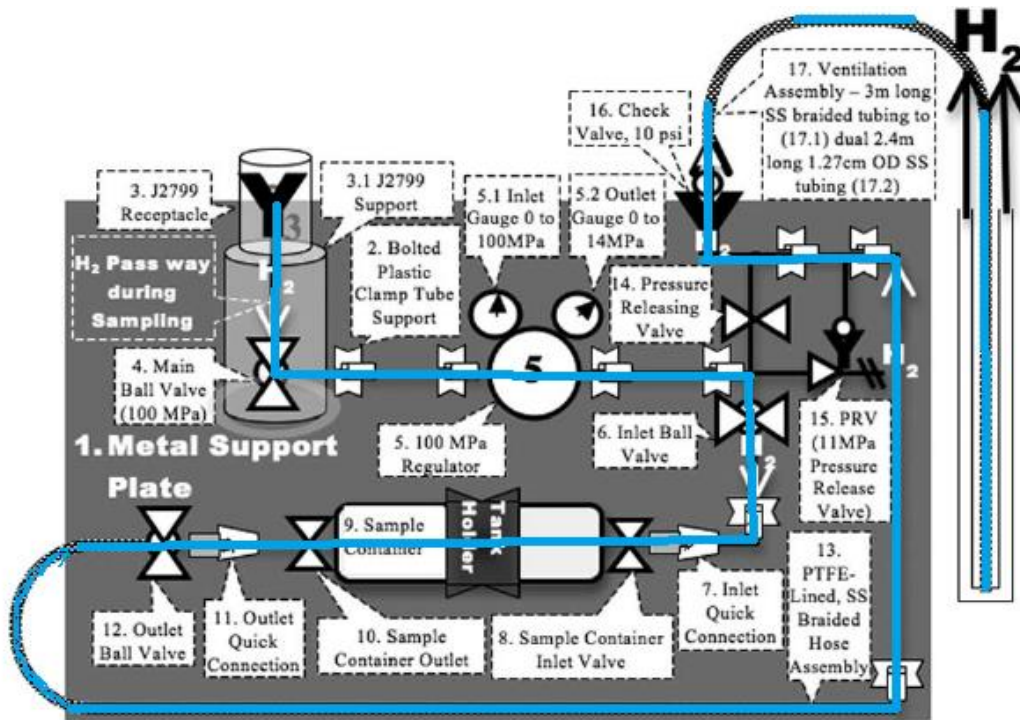
Series sampling does not require a vehicle.

The fueling nozzle is connected to a receptacle (J2799 (3)), positioned vertically, which can adapt to both 350 and 700 bar and which is rated at 700 bar (3). The receptacle is then connected to a main ball valve rated 1000 bar (4) which is connected to a reduction valve also rated at 1000 bar with a manometer (gauge) 0-1000 bar to monitor inlet pressure and a manometer 0-140 bar to monitor outlet pressure (5). The station leak test is performed before sampling to ensure that there are no leaks in the hydrogen fuel delivery system by closing the main ball valve (4) using the residual high pressure left in the station hose. The main ball valve has also the function to prevent failure of the regulator (5) due to rapid hydrogen pressurization. The main valve is slowly opened to prevent this from happening.

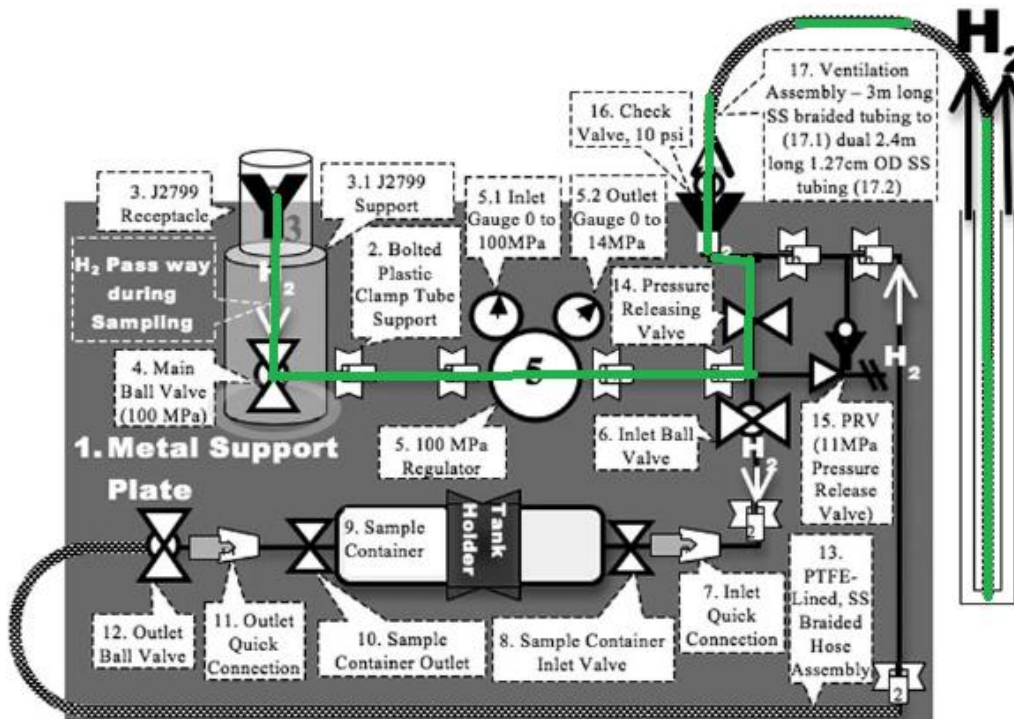
After the reduction valve, a 4 way cross is installed leading to:

- a) A pressure release valve (15) which opens if the main ball valve fails, to release hydrogen pressure above 103 bar
- b) A sample inlet ball valve (6). The sampling cylinder (9) is a two-ended valve cylinder with an inlet valve (8) and an outlet valve (10). The inlet ball valve and the sampling cylinder are connected with an inlet quick valve (7). The outlet ball valve (12) and the sampling cylinder outlet valve are also connected with a quick connector (11)
- c) Another pressure release valve (14): this valve is always closed before and during sampling. After sampling, the valve is opened before removal of the sampling cylinder to release the hydrogen pressure in the HQSA through a check valve (16) which prevents air from back

diffusion into the HQSA. To the check valve is connected a ventilation assembly consisting of a 3 m long SS braided tubing interfaced to a 2.4 m long SS tubing (1/1 inch. OD)



a



b

Figure 2: System used in series sampling: (a: gas flow during sampling, b: gas flow during release of the pressure after sampling)

5.3 - Available sampling devices

Several devices have been used to sample hydrogen. Some of the devices that have been used to sample hydrogen at HRS are shown in Figures 3, 4 and 5.



Figure 3: HQSA used in the HyCoRa project (parallel sampling)



Figure 4: HQSA used by Smart Chemistry [4] (series sampling)



Figure 5: HQSA used in Japan [5]

5.4 - Available sampling vessels

Currently, analytical laboratories usually provide a service that includes sending their own commercial sampling devices to the HRSs for filling.

The draft for standard ISO 19880-1 does not specify which cylinder to be used. It is mentioned that the sampling cylinder can typically be a 10 litre aluminium canister with a DIN477/1 connector, but no other specifications are mentioned. A one-ended valve cylinder is used in this case.

Standard D7606-11 (6.8) specifies that the sampling cylinder and the inlet and outlet valves of the cylinder should be passivated (internally coated with silicon) to minimize adsorption of sulphur species.

6 - Risk assessment sampling

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. An example of this would be an air leak in the system allowing ingress of oxygen and nitrogen into the hydrogen sample.

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.

6.1 – False positives (over-estimation)

6.1.1– Air leaks

Air leaks are another likely source of contamination that would lead to a false positive result. The ISO 14687-2 [7] levels of oxygen and nitrogen respectively are, $5 \mu\text{mol.mol}^{-1}$ and $100 \mu\text{mol.mol}^{-1}$. Therefore, a small ingress of air could lead to above specifications levels. 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 quality of measurements, it could lead to a hazardous scenario where hydrogen may directly blend with oxidising agent providing an oxyflammable mixture which if ignited would lead to explosion. To minimize this risk, the time between evacuating the sample vessel and taking the sample must be as short as possible.

6.1.2 – Water

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 on a separate feed of high pressure inert gas). As the ISO 14687-2 specification for water is set fairly low at $5 \mu\text{mol.mol}^{-1}$, even a small ingress of moisture contamination is likely to affect the purity. The same issues could occur if the sampling vessel is not evacuated or purged properly, there is guidance on this procedure in ASTM D7606-11 and in MetroHyVe report A4.1.3.

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 is leak tight will reduce the number of purge required.

6.1.3 – Carry-over

It is possible that impurities from a previous sample may remain in the sampling vessel (if a proper procedure for evacuating the vessel has not been used). This is particularly important if the sample had previously contained “sticky” compounds. Effective purging or evacuation of the vessel will avoid carry-over, and can be tested by refilling with pure hydrogen from a gas supplier and performing a full hydrogen purity test.

6.1.4 – Cleaning/purging

If cutting oils or cleaning products are used at any stage either during manufacture of the refuelling station or during maintenance, contamination from sulfur, hydrocarbons or halogenated is possible. This however should not be considered as a false positive as this would be a real impurity in the hydrogen.

6.2 – False negatives (under-estimation)

6.2.1 – Loss due to adsorption

Some of the impurities to be analysed have a propensity to adsorb on surfaces (adsorption in vessels and/or in sampling line (inclusive regulators)).

Sulphur species are reactive compounds with propensity to adsorb to the internal surfaces of sample vessels and transfer lines. Recently, the challenges of performing accurate analysis of low concentrations of Sulphur-containing compounds have been highlighted in a review focusing on the issues around sampling of these compounds [6]. The article focused on data obtained using synthetic gas standards of known composition.

Cylinders are usually treated by one or both of two approaches:

- Reducing the internal surface area of the cylinder (e.g by polishing) or,
- Passivation (e.g. by coating or chemically treating)

The use of an appropriate cylinder was found to be a crucial contributory factor to the stability of sulphur-containing compounds. It is not only the cylinder that is of importance but it is also essential that suitable sampling line materials are selected. A general consideration is that the total internal volume of the regulators and lines should be kept to a minimum as the internal surfaces and “dead volumes” within lines can cause losses of sulphur-containing compounds. Losses may also be dependent upon the flow rates.

It is specified in ASTM D7606-11 to use sampling cylinders and valves internally coated with silicon (Si) for the sulfur species.

6.2.2 - Reactions

Ammonia is a reactive gaseous compound due to its water solubility (31% w/w at 25°C), its polarity and its ability to adsorb/desorb on different materials. Ammonia adsorption/desorption effects have been studied for various materials and the conclusions were that the mechanisms of adsorption of ammonia is rather complicated and dependent upon many factors including the vessels material and/or the concentration, and the presence of water.

Formaldehyde is not considered thermodynamically stable in hydrogen. Decomposition of formaldehyde may happen due to surface catalytic effect. The by-product can be methanol, water or dimethoxymethane compounds. The effect is stringent at low amount fraction ($< 2 \mu\text{mol/mol}$).

The use of appropriate coating or online analysis will help with reactive compounds. Secondly it is important to perform the measurements as quickly as possible to avoid any under-estimation of the real content of ammonia or formaldehyde.

7 – Current recommendations

Both standards (ASTM D7606-11 and ISO 19880-1) propose specific purging procedures of the HQSA.

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 (Paragraph 6.7) to ensure a valid sample. This procedure 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 (Paragraph 9.2).

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 (Paragraph 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.

8 – Future work

This report outlines the current knowledge and standard practice for sampling hydrogen at the refuelling station, but more work (though both laboratory and field testing) is required to develop best practice guides for the hydrogen industry. The EMPIR Metrology for Hydrogen Vehicle project includes several activities for this purpose including:

- Purge cycle testing of hydrogen during sampling at a station
- Sampling vessel evacuation studies
- Validation of particle filter sampling
- Assessment of sampling when using adsorbent tubes
- Stability testing of hydrogen impurities in commercial available vessels

The studies above will provide the project partners with the required information to write good practice guides for the various aspects and challenges which will be freely available for hydrogen refuelling station operators and associates.

9 - References

- [1] ISO 19880-8:2017
- [2] Hydrogen Mobility Europe, H2ME
- [2] https://energy.gov/sites/prod/files/2015/04/f21/fcto_2014_hcd_workshop_1_report.pdf
- [3] <https://www.nrel.gov/docs/fy15osti/64063.pdf>
- [4] www.smartchemistry.com
- [5] ISO 19880-1 (draft)
- [5] ASTM D7606:1 including Annex 1, Sampling procedures and Hardware for Hydrogen Fuel Quality Analysis
- [6] Sampling of gaseous sulfur-containing compounds at low concentrations with a review of best-practice methods for biogas and natural gas applications, A.S. Brown, A.M.H. van der Veen, K. Arrhenius, A. Murugan, L.P. Culleton, P.R. Ziel, J.Li, Trends in Analytical Chemistry, 2015, 64, 42-52
- [7] ISO14687-2