METROLOGY for HYDROGEN VEHICLES 2

# REPORT:

## *A3.1.1 – A3.2.1: Review of the state of the art of gas sampling systems available and used at HRS*


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Report A3.1.1: Review of the state of art of gas sampling systems available and used at HRS

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## Summary

This report was written as part of activities A3.1.1 and A3.2.1 from the EMPIR Metrology for Hydrogen Vehicles 2 (MetroHyVe2) project. The three-year European project commenced on 1st August 2020 and focused on providing solutions to four measurement challenges faced by the hydrogen industry (flow metering, quality assurance, quality control, sampling and fuel cell stack testing). For more details about this project please visit https://www.sintef.no/projectweb/metrohyve-2/.


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# Contents

# 1 - Introduction

One method to control the quality of hydrogen fuel at a Hydrogen Refueling Station (HRS) is the so-called spot sampling (offline sampling). Spot sampling at a HRS involves collecting 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 is that a more detailed laboratory analysis can be performed on the sample using a large pallet of analysis instruments. The disadvantages are that the results are usually only available 1-2 weeks after the samples were collected and only provide a snapshot of the hydrogen fuel quality at the time the samples were collected.

Beyond the accuracy of the analytical method, taking a representative sampling is of high importance for the hydrogen industry as important decisions are based on the outcomes of the hydrogen quality assessment (i.e. decision to allow or stop refuelling public vehicles, HRS maintenance). The hydrogen quality assessment relies on a reliable and representative sampling procedure. This requires using appropriate sampling strategies and materials for the sampling devices and cylinders.

Currently, different strategies for the sampling of hydrogen fuel for quality assurance of gaseous species are implemented in different parts of the world and so far, these strategies have never been compared. However, it is of high importance to demonstrate that regardless of the strategy chosen, the outcomes of the hydrogen purity assessment are the same; i.e. in metrological terms are reproducible. Two metrological challenges are associated with the hydrogen fuel sampling:

- Is the sample taken representative of the overall process of the refuelling station or only part of it? This aspect will not directly be studied during the MetroHyVe2 project.
- Is the sample taken similar to the hydrogen fuel at the time of the sampling? The challenge is to ensure that the sampling and the transport process d not alter the sample. This aspect will be studied during the MetroHyVe2 project.

Several issues should be dealt with discrepancies in the results between two strategies (i.e. significant difference in results due to the sampling) and avoidance of the two scenarios where false results (negative or positive) could occur. 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, water 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 sampling vessel. This report intends to review the state-of-art of these different strategies including the following steps:

- The choice of sampling method (parallel or series) including the components of the sampling device
- The choice of the sampling vessels (size, material, treatment, valves)
- The different requirements in term of filling pressure, safety, connection fitting
- The procedure to prepare the sampling vessels before sampling (cleaning strategy)
- The procedure to purge the sampling device (for instance to remove air and water)

There are currently at least two standards that describe sampling strategies at a HRS. In the standard ASTM D7606, one strategy (“gas serial”) is presented. In the standard ISO19880-1:2020, annex K [1], three strategies are currently mentioned: “gas parallel”, “gas serial” and “gas direct”.

In this report, the strategies are defined as:

"Gas parallel": in this strategy, a tee-connection is used to parallelly fill the sampling cylinder and a FCEV or a receptacle (larger than the sampling vessel) from the HRS nozzle

"Gas serial": the strategies "gas direct and "gas serial" have been merged in this report as they are following the same concept. In these strategies, the sample is taken from the HRS nozzle directly into a sampling cylinder only. For these methods, the sampling system must be able to manage the hydrogen fuel conditions from the nozzle and may require operating the HRS in service mode.

Most of the strategies presented in this report obtain samples for offline analysis by filling cylinders only. However, some strategies also allow a limited onsite quality assessment (for example online analysis of water and oxygen).

# 2 – Methods for sampling at the nozzle

## 2.1 - "Gas serial" methods

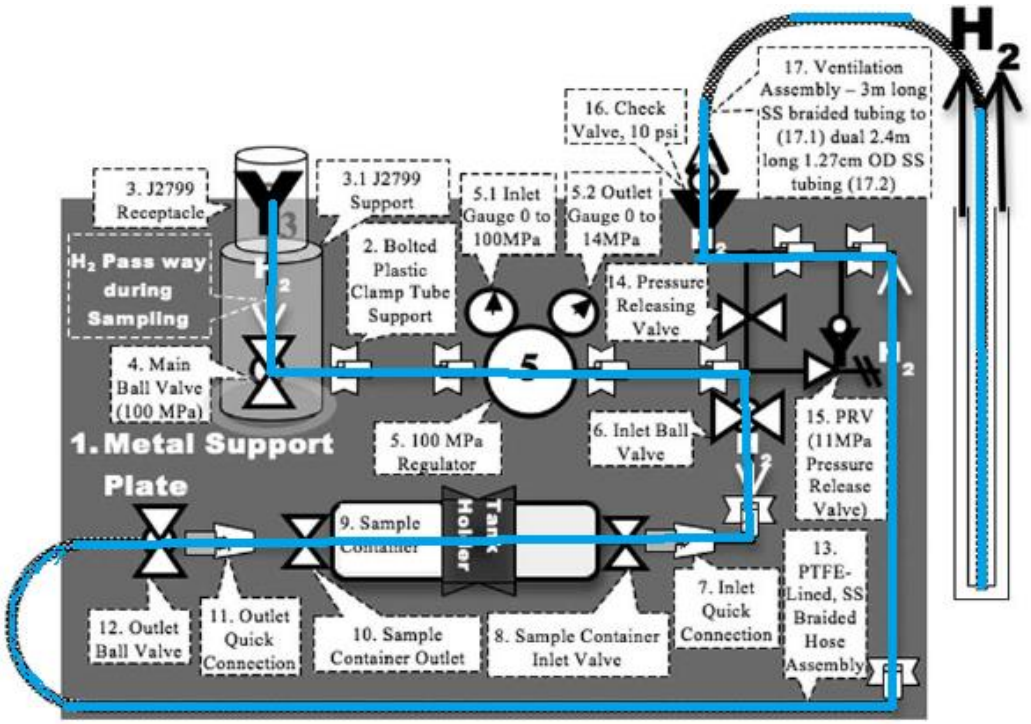
This section will present the different "gas serial" methods currently available. All these methods follow the same root principle, the sample is taken from the HRS nozzle directly into a sampling cylinder. In these methods, the sample cylinder is often a double-ended valves cylinder as the hydrogen is filled in series from the nozzle. However, if a tee-connection is installed just before the cylinder, a single-ended valve cylinder can be used.

There are currently four "gas serial" sampling methods or systems: ASTM method, Air Liquide´s method, gas direct method and ENGIE´s method.

### 2.1.1 – ASTM method

This method is currently used in USA by companies conducting hydrogen fuel quality audits and is described in the standard ASTM D7606-17. The sampling is performed at the nozzle and venting of hydrogen to atmosphere is performed through an exhaust stack. The sampling device is referred to as HQSA (Hydrogen Quality Sampling Apparatus). The method works for stations delivering hydrogen at 350 and 700 bar.

The components of the sampling device are presented on Figure 1 which is taken from the ASTM D7606-17 standard. The gas path is indicated in blue for filling of the cylinder and in green for venting of the device after sampling.

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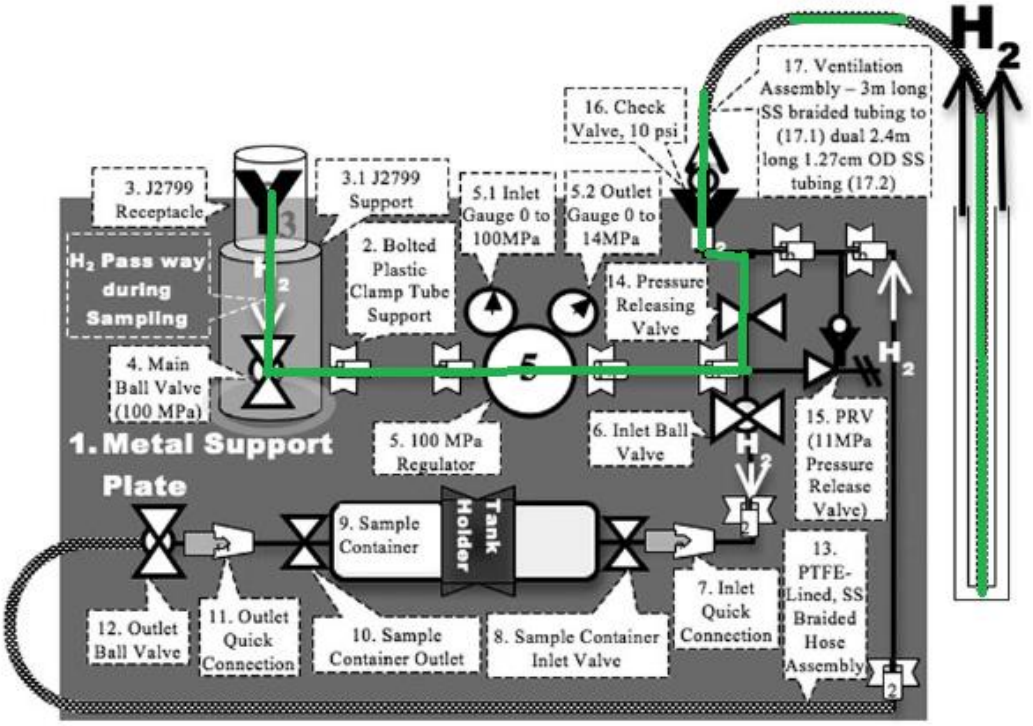


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*Figure 1: D7606-17 sampling device (a: blue line gas flow during sampling,*

*b: green line gas flow during release of the pressure after sampling)*

The fuelling 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 at 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 pressurized gas 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 happening.

After the reduction valve, a four-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 to an quick connection (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 in the HQSA though a check valve (16) which prevent air from back diffusing into the HQSA. The check valve is connected to a ventilation assembly consisting of a 3 meters long SS braided tubing interfaced to a 2.4 meters long SS tubing (1/1 inch. OD)

The sampling cylinder is a two-ended valve cylinder. Standard D7606-17 (6.7) 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. The inlet ball valve and the sampling cylinder are connected to an inlet quick valve. The volume of the cylinder is 1 liter and the cylinder is filled at a pressure of 69 bar.

In standard ASTM D7606-17, 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.

Eventual traces of water are removed during the cleaning procedure of the sampling device. The HQSA must be cleaned by purging before taking the sample. This is done by flowing 1 kg of hydrogen fuel through the HQSA after the nozzle pressure is regulated to 69 bar so the hydrogen flow rate is approximately 33.3 g/s for a total sampling time of 30 seconds. The procedure aims at removing traces of moisture in the HQSA, sampling line and sampling cylinder.

Airborne laboratories have developed a commercial sampling device (called NSP-7606) compliant to ASTMD7606-17. It comes with 10-meter flexible line connected to the vent system of the HRS or a tripod for atmospheric ventilation. It is also possible to install detector tubes (such as Draeger tubes or similar test tubes) for onsite screening of some impurities listed by SAE J2719. Pictures of the device are presented on Figure 2.


***Figure 2: NSP-7606 sampling device***

Documented use of the device has not been found as of the publication date of this document.

### 2.2.2 – Air Liquide method

Air Liquide has developed a modular sampling device (Figure 3) to sample at the nozzle in small cylinders. The sampling system has two functions: it allows to control the humidity onsite and to sample hydrogen to perform quality control of all other parameters offline. The device includes quick connections, modules with pressure regulators and manometers, mobile vents. No vehicle is required for the system.

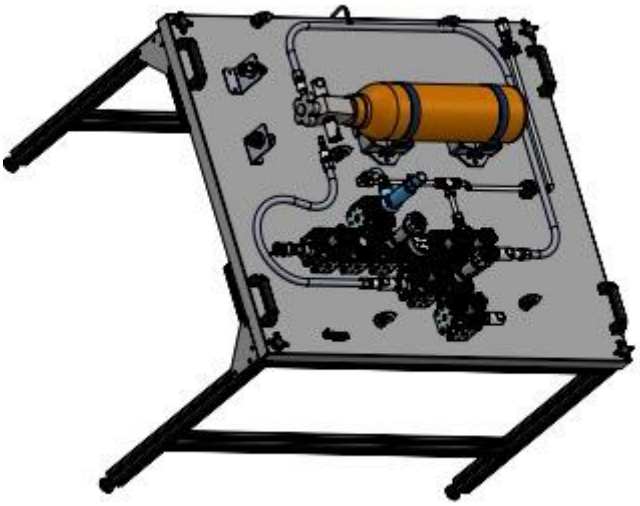

*Figure 3: Air Liquide sampling system*

The sampling cylinder is a two-ended valve 5-liter cylinder in aluminium with stainless steel valves and is filled to 150 bar (no specific treatment). The cylinders undergo a four steps cleaning procedure at the laboratory. The cylinders are first emptied then filled with nitrogen. The cylinders are then rinsed with a minimum of five cycles with pure hydrogen and then filled with residual hydrogen to around 5 bar.

Certain specifications must be followed in order to avoid any incident regarding the safety risks:

1. The device is directly connected to the station's vent or is equipped with a portable vent pipeline
2. The sampling device connected to the nozzle is equipped with an anti-whip cable (pressure risk)
3. The flexible pipes connected to the sampling cylinder are equipped with an anti-whip cable (pressure risk)
4. The flow network is equipped with a check valve connected to the portable vent system or to the station's vent (pressure risk)
5. Each vessel is equipped with a check valve and engraved with the letter "H" to respect the European agreement concerning the carriage of Dangerous Goods for transport rules (pressure risk)
6. The full device is connected to electric ground to avoid any electrostatic discharge (electrical risk).

Before filling the vessel, the sampling device is purged by applying pressurisation and venting cycles and a leak test is applied. The device is also containing a second parallel stream able to host a portable analyzer (usually a moisture controller) which can be used during the purge or sampling phase (static or dynamic mode).

For the dynamic filling mode the vessel is purged by applying a pressurisation and venting protocol, (inlet vessel's valve is opened) while for the static filling mode the vessel is purged by applying a continuous flow (inlet and outlet vessel's valve are opened).

When all parameters are reached (number of pressurisation and venting cycles, duration of purge, moisture concentration) the vessel valves are closed (inlet and outlet valves depending on the filling mode used) and the sampling device is unpressurized to the vent pipeline to reach the atmospheric pressure.

### 2.2.3 – Gas direct method

This method is currently used in Japan and is described in ISO19880-1 Annex K. In this standard, this method is considered as an alternative to gas serial and gas parallel methods but in practice, from the information available, the method is related to a "gas serial" method with single-ended valve cylinder.

The sampling device consists of a receptacle (1), decompression measure as pressure regulator (2), safety measures as safety relief valves (3) and a sampling cylinder (4). It also contains a pressure sensor and a temperature sensor positioned and operated near the gas cylinder for safety reasons. The components of the sampling device are presented in Figure 4 which is taken from ISO19880-1 [1].

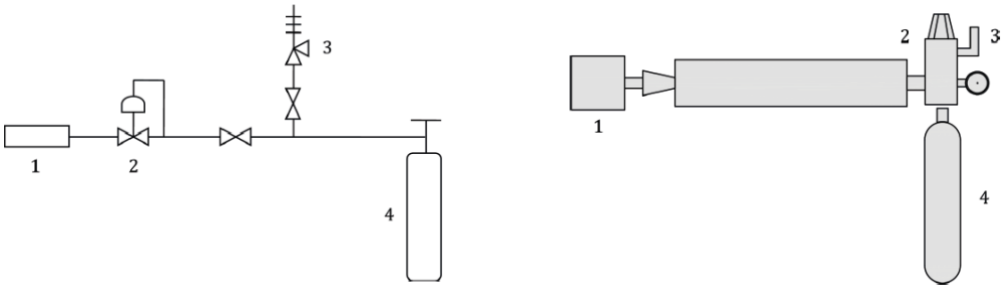


*Figure 4: "Gas direct" sampling device*

A provider of cylinders used in Japan for this sampling system is Benkan Kikoh [6]. For hydrogen, the cylinder is made of manganese steel and the volume is 46.7-liter (this provider can also supply cylinder with a volume of 40-liter). The cylinder series called "SUMI-FINE" has polished inner surface. The valves of the cylinders (type DSP21) are made of stainless steel (from Neriki).

In ISO19880-1 Annex K, no sampling pressure is indicated. It is only stated that the sampling is stopped when there is enough hydrogen in the cylinder. However, the cylinders from Benkan-Kikoh [6] has a maximal capacity pressure of 147 bar. The cylinders are usually filled with less than 120 bar.

The sampling cylinder is prepared by purging with pure hydrogen (backfill) and then evacuated ("hard" vacuum). Onsite, the sampling cylinder is purged with the hydrogen to be sampled.

The sampling adapter and sampling cylinder are purged through the vent system assembly. Typically, 1 kg of hydrogen is used for the purge. At the start of sampling, the sample cylinder outlet valve is closed to fill the cylinder.

### 2.2.4 – ENGIE sampling device

ENGIE has developed its own method for hydrogen sampling and online analysis of oxygen and water during a refuelling event. The sampling is performed at the nozzle without overriding the safety protocol of the station nor using a vehicle. This is achieved due to a mobile sampling device equipped with a 55-liter tank to simulate a FCEV car.

The sampling device (Figure 5) is composed of three inlets; two different inlets to connect to HRS 350, 350HF (high flow) and 700 bar. A third inlet is dedicated to the sampling and preparation (pre-filling of the tank which is necessary to stabilize the tank) before refuelling. This inlet is also used to flush the device with nitrogen after sampling to remove hydrogen before transportation.

The sampling device is also composed of three different lines:

Line A: A 55-liter tank simulating the presence of a FCEV allows to perform a refuelling protocol (no safety bypass) with hydrogen from the HRS

Line B: this line is dedicated for the online analysis of oxygen and water using an optical laser spectroscopy analyser. This offers the possibility to get real-time information on hydrogen quality and detect any changes during refuelling. A fast loop enables to refresh continuously the gas sample during the refuelling. Moreover, pure hydrogen is used before the analysis (during the refuelling) in order to establish blank levels.

Line C: this line allows spot sampling in a 1-liter coated stainless steel cylinder filled with 90 bar. During sampling, the cylinder is flushed with the equivalent of more than 10 times its volume. Before sampling, the cylinder is cleaned at the laboratory by flushing with nitrogen. A residual pressure of 500 mbar is maintained before sampling.

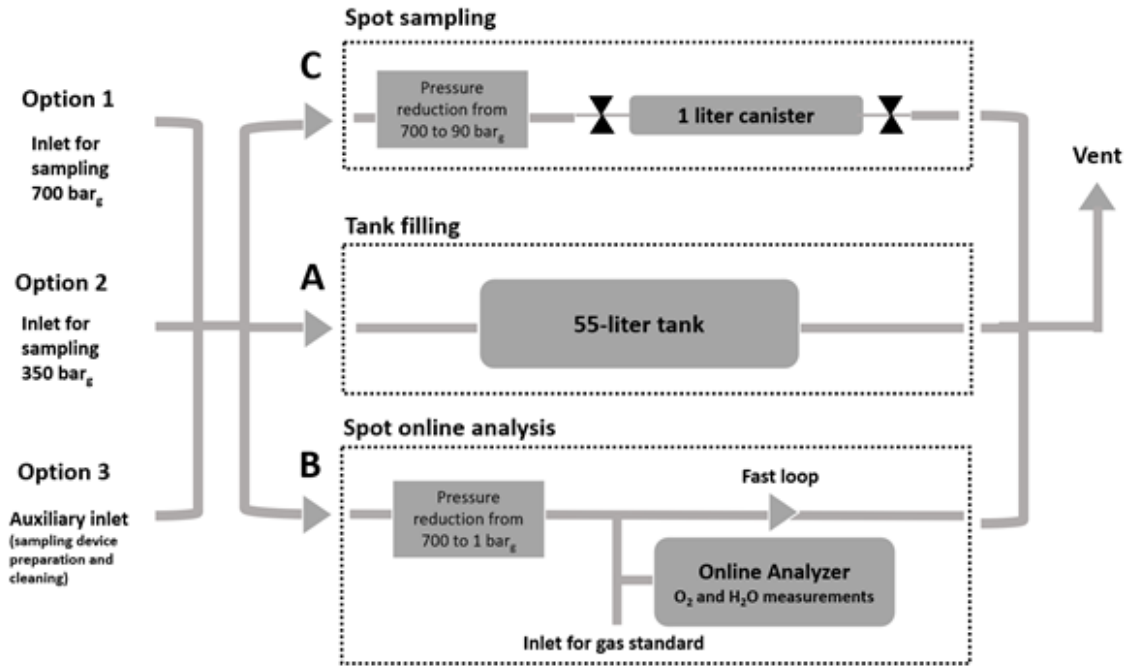


*Figure 5 - ENGIE sampling device*

## 2.2 – Method "gas parallel"

This section will present the different "gas parallel" method currently available. All these methods are following the same principle; a tee connection is used to parallelly fill the sampling cylinder and a FCEV or a receptacle (larger than the sampling cylinder) from the HRS nozzle.

For these methods, a tee-connection is used to parallelly fill the sampling cylinder and a FCEV vehicle.

This method is currently applied in Europe using Linde Qualitizer by companies such as SINTEF, LINDE and NPL and is succinctly described in ISO19880-1 annex K [1]. ZBT has also developed a system for "gas parallel" sampling called Hy-SaM which stands for hydrogen Sampling Module). The method follows ISO19880-1.

### 2.2.1 – Methods using the LINDE Qualitizer

The sampling is performed using a tee fitting called the Qualitizer manufactured by LINDE. The components of the sampling device are presented on Figure 6 which is taken from ISO19880-1 [1].

The sampling device consists of a tee fitting (5), a vehicle and receptacle (6), a sampling cylinder with a pressure regulator and a pressure relief valve (1,2,3).

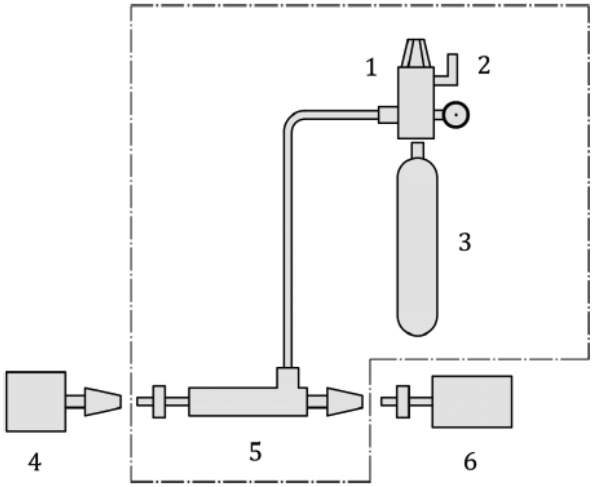


*Figure 6 - "Gas parallel" sampling device from ISO19880-1*

The sampling cylinder is 10-liter aluminum with a single-ended standard DIN 477 No1 stainless steel valve. LINDE and NPL use SPECTRA-SEAL® cylinders (BOC, UK). The treatment consists of a proprietary process that renders the aluminium surface chemically inert. Additional processes convert the passivation layer into a surface with negligible adsorptive properties [3].

For the method with the Qualitizer, a requirement is the availability of a vehicle having an almost empty tank [4] so the refuelling process is long enough to achieve at least 50 bar in the 10 liter cylinder. The pressure is limited by the pressure reducer to a maximum of 150 bar. The coupling of the sampling and refuelling of a car takes 3 to 5 minutes. The cylinder must have a DIN477 No1 valve to fit the Qualitizer system.

Different procedures are in use to prepare the sampling vessels before the sampling.

- Pressure swing purges at elevated temperature with inert gas (He, $N_2$) with subsequent evacuation: this procedure is used by LINDE
- Pressure swing purges with UHP (Ultra High Purity) hydrogen and evacuation to 1 mbar. The procedure for purging adapted by SINTEF in the HyCoRA project has been to evacuate 10 L, spectra-seal cylinders to 1 mbar, followed by pressurization to 10 bar with UHP hydrogen. This procedure was repeated tree times before the cylinders was finally evacuated to 1 mbar prior to sampling use. The choice of pressure levels and repeat cycles was chosen arbitrary and has not been evaluated with respect to performance. The SINTEF approach has not been validated at the laboratory but has been evaluated to be sufficient for some compounds based on several campaigns where more than 40 samplings at HRSs were performed and no evidence of carry-over from one sample to the next has been observed. In the case of a violation of fuel quality it was investigated if there was any carry-over to the next sample.
- Evacuation to high vacuum (1 x $10^{-6}$ mbar): NPL developed a method in seven steps. The procedure is explained in detail in the report A4.1.7 [5] and requires the use of a roughing pump, a turbo pump and residual gas analysis combined into a 'evacuation rig'. The roughing

pump is used to partially evacuate the cylinder (around 1.1 x $10^{-1}$ mbar or less) and the evacuation is subsequently done using the turbo pump (1 x $10^{-7}$ mbar). The outgassing of air, moisture and any remaining contaminants is monitored on the residual gas analyser. If an expected impurity remains within the system this should be removed by heating or including a subsequent hydrogen purge step.

To ensure the absence of contaminants in the sampling system, several purging procedures have been applied. In ISO19880-1 Annex K, two procedures are proposed to purge the Qualitizer sampling device:

1) By initiating a sampling but aborting within 15 seconds in order to isolate the test pulse and then depressurizing the sampling device with the bleed valve. The procedure is described in detail in [4].
2) By performing the operational procedure without connecting the sampler to FCEV (HRS safety will shut off hydrogen dispensing) and depressurizing with the bleed valve prior to attaching to the FCEV receptacle and performing the operational procedure for gas sampling.

A third purging procedure has been developed by NPL during EMPIR project MetroHyVe1 using prefilled sampling cylinders. The procedure is explained in detail in the report A4.1.7 [5]. This approach uses 10 litre cylinders that have been pre-filled with ultra-high purity (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. The procedure requires to use a correction factor to account for the dilution due to the hydrogen in the cylinder.

### 2.2.2 – Hy-SaM sampling system

The method developed by ZBT and ZSW [7] (Figure 7) offers the possibility to sample in one to three cylinders simultaneously and also to sample for particulates simultaneously. It also offers the possibility to use a buffer tank rather than using an FCEV. The safety relief valve, the depressurization of the system and optional depressurization of the buffer tank are led to a mobile vent (alternatively to the HRS venting line).

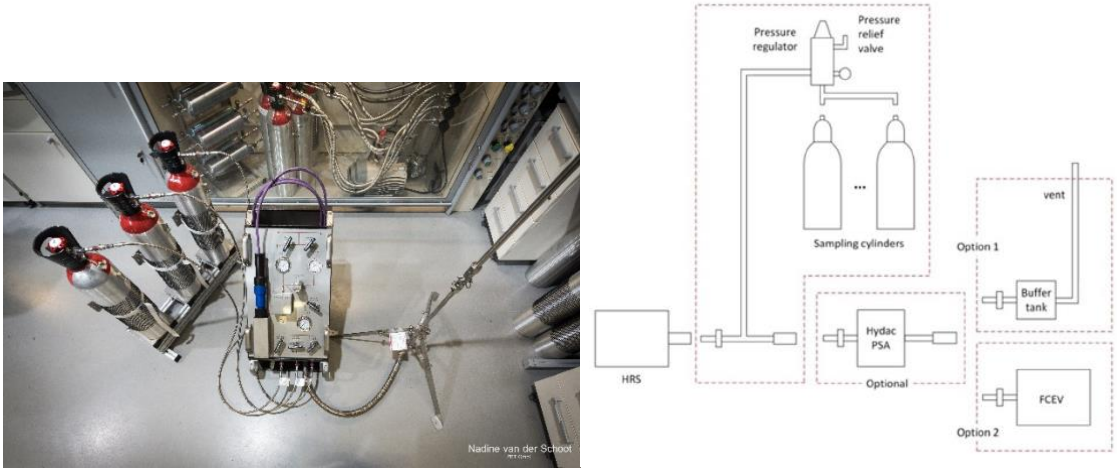


*Figure 7 - Hy-SaM sampling device*

The cylinders are 2.25-liter stainless steel cylinders (sulfinert 2000 coated). or 10-liter aluminium single-ended valve (Spectra-seal treated DIN 477 N.1) cylinders. The cylinders are usually filled to about 90 bar.

The cylinders are previously evacuated down to $10^{-7}$ mbar with a turbopump. The cylinders can be used evacuated or are pressurized with 300 mbar high purity hydrogen (Purity 9.0). The argument for using a slight over-pressure is to avoid contamination by air.

# 3 – Safety and hydrogen venting

It is critical that all the sampling equipment for hydrogen fuel sampling at the HRS nozzle complies with local and international regulations. They should be operated by trained staff and follow regular maintenance and audits to ensure the safety of the system while in operation.

A critical aspect of hydrogen fuel sampling is the venting of hydrogen prior, during and after the sampling event. As explained when describing the different strategies, it is required to purge several times the sampling system with large volumes of hydrogen (i.e. 1 kg), or at various locations of the sampling system (i.e. purge valve of the Qualitizer). Therefore, an important aspect to consider is how to perform hydrogen venting safely at HRS during a sampling event.

It may be required to ensure that a mobile vent is used. It is important to ensure that the position of the mobile vent is agreed with the HRS operator for health and safety considerations. All systems have pressure relief valves, these safety valves may require to be connected to a safe vent. Otherwise, the hydrogen released in event of an incident will be close to the nozzle with risk associated to the ATEX zone.

Another possibility would be to connect sampling systems to the HRS safety vent. In this case, it would be important to standardize the connection to the HRS safety vent.

# 4 – Methods for sampling at other locations

Additional sampling strategies have been developed and used for sampling hydrogen fuel from other locations than the HRS nozzle. This section will present these sampling procedures that are available for additional locations (i.e. hydrogen production or various parts of the supply chain).

## 4.1 – LINDE sampling strategy

LINDE has developed a sampling strategy without the Qualitizer. This sampling strategy is applied at HRS with separate sampling point. The procedure is shown in Figure 8. In this case, the sampling cylinder is a 10-liter aluminium cylinder with a double-ended valve with a dip tube. The valves are DIN477 No1 valves.

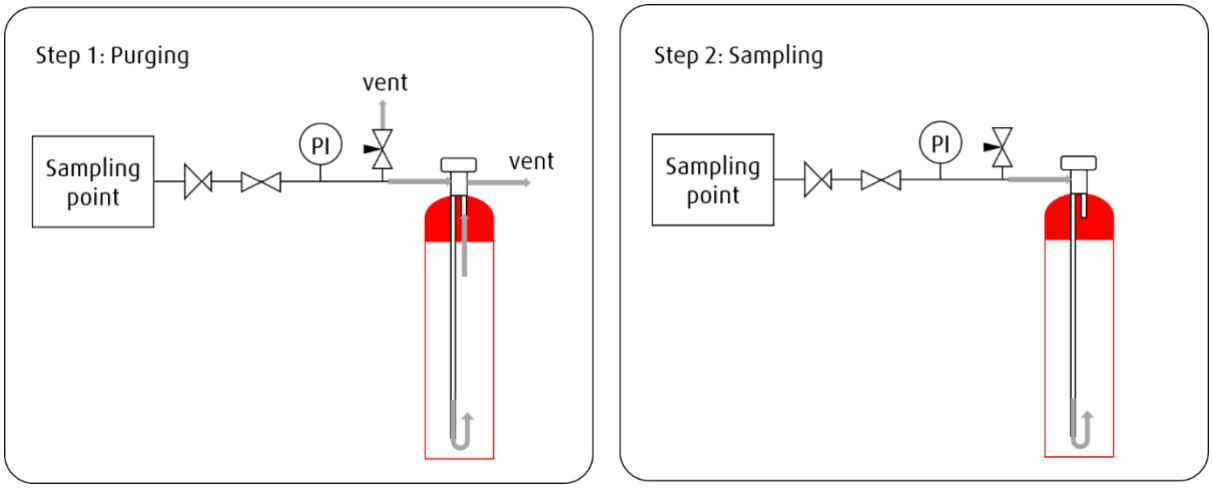


*Figure 8 – Alternative LINDE sampling strategy*

The sampling cylinder is previously cleaned and evacuated at LINDE facilities using repeated pressure swing purges at elevated temperature (60ºC) with nitrogen and helium. After the pre-treatment, the cylinder is filled with helium to up to 0.5 bar (overpressure) and subsequent evacuation. The sampling pipeline and the sampling cylinder are purged at the HRS. The targeted pressure for the sampling procedure depends on the volume needed for the analysis. In general, the filling pressure is between 50 to 150 bar.

### 4.2 - Hydrogen sampling at low-pressure

Another low-pressure sampling rig has been described by Bacquart *et al*. for sampling at hydrogen production facilities [4]. 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, a filling line with two check valves 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 parts of stainless steel 316 grade. The sampling rig can be used with various type of cylinders from stainless steel 1 to 4-liter vessels to larger cylinders (i.e. aluminium cylinder 10-liter 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. The sampling procedure involves sampling rig cycling purges (7 times) then double-ended valve cylinder pressure swing purges (7 times). The purging protocol achieved to remove any water contamination even from a contaminated sampling vessel.

## 5 – Considerations for reactive species

For reactive species, special precautions may need to be accommodated when sampling. Some treatment of the inner surface of the sampling cylinder may be needed. However, due to the large number of reactive species including in the standard ISO14687:2019, it may prove difficult to find one specific treatment that would work for all species. Another precaution can be to shorten the time

between the sampling day and the analysis day as decay is often time dependent. However, in some cases, decay can occur within 24 hours after the sampling.

During EMPIR MetroHyVe 1, two activities looked at the state-of-art for storage of impurities in cylinders:

Both reports (A2.3.1 [8] and A4.4.1[9]) have gathered information from stability studies performed over periods of time. While the preparation of primary gas mixtures requires long-term stability (at least several months), the time perspective for sampling is much shorter, it can be expected that the sample arrives at the laboratory within a time period of 1-2 weeks, maybe longer (up to 1-3 months) if collected outside of Europe.

In the report "A2.3.1 Review of the available passivation treatments for gas cylinders" [8], a review of the available passivation treatments for gas cylinders was done. This report focused on cylinders for standards (for example primary reference material). In this report, impurities were classified as non-critical (total hydrocarbons, helium, nitrogen, argon, carbon dioxide), critical (water, >C7 hydrocarbons, oxygen, carbon monoxide, or very critical (total sulphur compounds, formaldehyde, formic acid, ammonia, total halogenated compounds.

For non-critical species (total hydrocarbons, helium, nitrogen, argon, carbon dioxide), most available cylinder treatments were expected to perform in an acceptable way.

For critical species, adsorption and/or stability issues are expected, and very critical species are known to be reactive impurities. For these impurities, the challenges are numerous. For example, experiment with 10 µmol/mol of formaldehyde in a Spectraseal cylinders showed decay with time that was dependent on the Spectraseal cylinder itself, showing that a careful selection of cylinders is pre-requisite. However, more than 80% stability over a month was achieved in Silconert 2000, Sulfinert and Performax cylinders for formaldehyde at 1 ppm in hydrogen. Even in Aculife VIII, the stability was good at 500 nmol/mol. Formic acid in hydrogen was found to be stable in Spectraseal cylinders at amount fractions of 50 and 100 µmol/mol but instable (over a 3-months period) at 0.3 µmol/mol. Another issue that was raised is the possible interaction between species or with hydrogen. For example, oxygen in hydrogen may form water which is another impurity to analyse.

A literature review was done regarding the state-of-art for the storage of reactive species for the purpose of sampling in vessels [9]. Sulphur compounds (specifically $H_2S$) have been studied in larger extents than formaldehyde and formic acid. However, most of the results (in aluminium or steel cylinders) show that passivation was required when storing impurities as sulphur compounds and ammonia. When hydrogen sulphide was stored in a non-treated cylinder, fast decay was observed. For example, at a concentration of 0.5 µmol/mol, half of the hydrogen sulphide was lost in a period of 10 days when stored in acid washed aluminium alloy cylinders or basic aluminium alloy cylinders while the decay was much slower in "superior gas stability" cylinders. An initial loss of around 20% was observed in these cylinders but after this loss, the concentration remained stable for at least 100 days. At a concentration of 17 nmol/mol, hydrogen sulphide was totally lost after one day when stored in non-treated stainless-steel cylinders while hydrogen sulphide concentration remained stable for a period of at least 7 days when stored in SilcoNert 2000 coated cylinders.

Some stability studies were conducted during the MetroHyVe1 project (report A4.4.5 [10]). The studies were performed using gas mixtures containing two impurities and at levels that are relevant for hydrogen purity testing. SilcoNert 2000-treated stainless-steel cylinders and Aculife IV-treated aluminium cylinders were filled with hydrogen gas mixtures containing 100 nmol/mol HCl and 100 nmol/mol CO and 400 nmol/mol HCl and 400 nmol/mol CO respectively. Spectraseal-treated

aluminium cylinders and untreated aluminium cylinders were filled with a hydrogen gas mixture containing 40 nmol/mol $H_2S$ and 110 nmol/mol CO. Dursan, Sulfinert and an untreated stainless-steel cylinders were filled by decantation from the untreated aluminium cylinders 6 months after the preparation of the original mixture (40 nmol/mol $H_2S$ and 110 nmol/mol CO). Stability issues were clearly observed for HCl and $H_2S$ (where some initial losses were observed). CO was found to be stable in all types of cylinders tested in these stability studies. However, when CO and HCl were both present in a hydrogen gas mixture, some initial losses were observed. The short-term stability studies for $H_2S$ were performed at concentration 10 times higher than the ISO 14687:2019 threshold. Even at this level, some initial losses were observed. It can be anticipated that similar or greater losses could be expected at even lower amount fractions (closer to the threshold). An almost total loss of $H_2S$ was observed when filling a Dursan treated stainless-steel cylinder.

The literature studies showed that there is very limited data available for hydrogen; the information provided in these reports [8,9] also included stability data obtained in matrices such as air or nitrogen and in some cases, biogas. Another conclusion was that the stability tests were done using different vessels sizes and configurations, at concentrations often largely above the threshold values for these impurities in the ISO 14687:2019 standard and that some of the information (about tests conditions) are missing. MetroHyVe 1 achieved to provide new technical evidence on some of the critical species ($H_2S$, HCl and CO). The study demonstrated that $H_2S$ and HCl were unstable in the cylinders tested due to initial loss. The observation of initial loss of critical species due to the cylinder type is a major challenge as it raises concern on false negative results of analysis (measured value lower than real value). On the other hand, the MetroHyVe study demonstrated the stability of CO in the different cylinders tested supporting the reliability of the sampling for this critical species.

MetroHyVe 2 work package 3.1 activities will provide much needed information on cylinder suitability by performing new stability studies in different sampling cylinders in order to support better practices in hydrogen fuel industry.

# 6 – Overview of the different strategies

In the Table 1, the different characteristics of the sampling strategies are summarized:

**Table 1. Sampling strategies characteristics**

| | Gas serial | | | | Gas parallel | |
|---|---|---|---|---|---|---|
| | **Air Liquide** | **ASTM D7606:17** | **Gas direct** | **Engie Device** | **Linde qualitizer** | **Hy-SaM** |
| Equipment (sampling device | Quick connections, modules with pressure regulators and manometers, mobile vents and allows sampling without vehicle and safety measures. | Receptacle, main ball valve, manometers, reduction valve, 4 way cross, pressure release valves, sampling cylinder, cylinder inlet and outlet valves, inlet and outlet quick valve, quick connection, check valve | Receptacle, decompression measure), safety measures, sampling cylinder (T, P monitoring) | Three lines for spot sampling, online analysis of $O_2$ and $H_2O$ and a line with a 55- liter tank to simulate a FCEV car | Tee-fitting , vehicle and receptacle, sampling cylinder, pressure regulator, pressure relief valve | Tee fitting, sampling cylinder(s), pressure regulator, pressure relief valve |
| **Sampling vessels** | | | | | | |
| | **Air Liquide** | **ASTM D7606:17** | **Gas direct** | **Engie Device** | **Linde qualitizer** | **Hy-SaM** |
| Size and configuration | Two-ended valve cylinder of 5-liter | Two-ended valve cylinder of 0.5-2 liter | One-ended valve cylinder of 47 liter | Two-ended valve cylinder of 1 liter | One-ended valve cylinder of 10 liter | One-ended valve cylinder of 2.25-liter or 10-liter |
| Materials | Aluminium (cylinder)/ stainless steel (Valve) | Stainless steel | Manganese steel | Stainless steel | Aluminium | Aluminium/Stainless steel |
| Treatment | | Internally coated with silicon | Polished | Coated (Sulfinert) | Ex: SPECTRA-SEAL | Spectra-seal/Sulfinert 2000 coated |
| **Requirements** | | | | | | |
| | **Air Liquide** | **ASTM D7606:17** | **Gas direct** | **Engie Device** | **Linde qualitizer** | **Hy-SaM** |
| HRS override | manual operation | yes | yes | no | no | no |
| Filling pressure | ~150 bar | 69 bar | < 12 bar | 90 bar | 90-130 bar | ~90 bar |
| Sampling duration | A) < 1 min / cylinder<br>B) ~ 30min / installation | < 1 min /cylinder | | | < 3 min | < 3 min |

| | | | | | | |
|---|---|---|---|---|---|---|
| Maximum rated pressure | 200 bar | | 147 bar | | 160 bar | 90 bar |
| Connection fitting | Quick connection fitting | Quick connection fitting | - | | Hose quick connects | Quick connection fitting |
| Venting | Yes (mobile or HRS) | yes | yes | | no (FCEV) | no (FCEV) |
| **Preparation procedures** | | | | | | |
| Cylinder Cleaning procedure (lab) | Standard cleaning procedure (on site) Several compression relaxation<br><br>Initial cleaning procedure for each new sampling cylinder or for those from a previous sampling with an excessive amount of impurities (lab)<br>1) Emptying<br>2) Steaming with N2<br>3) Rinsing with H2 (minimum 5 cycles)<br>4) Filling with H2 residual (pressure ~ 5 bar) | | The sampling cylinder is prepared by pulling a hard vacuum after a pure hydrogen backfill. The sampling cylinder is purged with the hydrogen to be sampled | The sampling cylinder is cleaned with nitrogen. A residual pressure of 500 mbar is maintained in the cylinder | Several procedures exist: ex: repeated pressure swing purges at elevated temperature with nitrogen and helium with subsequent evacuation (LINDE) | The cylinders are previously evacuated down to $10^{-7}$ mbar with a pump. The cylinders can be used evacuated or are pressurized with 300 mbar hydrogen. |
| Cylinder cleaning procedure onsite | | Together with the sampling device | Together with the sampling device | Together with the sampling device | no | no |
| Procedure to purge the sampling devices | | With 1 kg hydrogen through the device | With 1 kg hydrogen through the device | So as 10 times the volume of the cylinder is purged | Several procedures exist: ex: By Initiating a sampling/aborting/depressurizing or by performing the operational procedure without connecting the sampler | ?? |

# 7 – Summary of the suitability of cylinder

In Table 2, an attempt to summarize the results from the different stability studies is done. It is important to notice that the evaluation is based on results not always performed in a hydrogen matrix. The time-period of testing is not standardized so some studies were performed over months while others were performed over weeks. Finally, the definition of the term "suitable" would need to be defined quantitatively which is not the case in these studies. Finally, results from different studies using the same type of cylinders reach different conclusions.

**Table 2 – Cylinder suitability**

| | Untreated Stainless steel | | SilcoNert 2000-treated stainless-steel | | Untreated aluminium | | Aculife VII | | Performax | | Spectraseal | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | a | b | a | bs | a | bs | a | bs | a | bs | a | bs |
| TC | X | X | X | X | X | X | X | X | X | X | X | X |
| He | X | X | X | X | X | X | X | X | X | X | X | X |
| $N_2$ | X | X | X | X | X | X | X | X | X | X | X | X |
| Ar | X | X | X | X | X | X | X | X | X | X | X | X |
| $CO_2$ | X | X | X | X | X | X | X | X | X | X | X | X |
| CO | i.d. | S | i.d. | S | i.d. | S | i.d. | i.d. | i.d. | i.d. | i.d. | S |
| $H_2S$ | i.d. | I/S | i.d. | I | i.d. | I | i.d. | I | i.d. | i.d. | i.d. | I |
| HCl | i.d. | i.d. | i.d. | I | i.d. | i.d. | i.d. | I | i.d. | i.d. | i.d. | |
| $CH_2O$ | i.d. | i.d. | i.d. | S* | i.d. | i.d. | i.d. | i.d. | i.d. | S* | i.d. | I |
| $CH_2OH$ | i.d. | i.d. | i.d. | i.d. | i.d. | i.d. | i.d. | i.d. | i.d. | i.d. | I | S |
| $NH_3$ | i.d. | i.d. | i.d. | i.d. | i.d. | i.d. | i.d. | i.d. | i.d. | i.d. | i.d. | i.d. |

a: at ISO14687:2019 threshold
b: at Higher concentrations
X: should be suitable
S: suitability demonstrated (* more than 80% stability)
I: Issues were found (ex. of issues: need careful selection of the cylinder, initial loss…)
i.d.: Insufficient data

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