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Review Article

Strategies for the sampling of hydrogen at refuelling stations for purity assessment

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HIGHLIGHTS

- Detailed description of different strategies for sampling hydrogen at the nozzle.
- Discussion on the representativeness of the sample collected.
- Results from different stability studies for gaseous species in different cylinders.
- Highlight the need of comparative studies to assess equivalence between strategies.

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ABSTRACT

Hydrogen delivered at hydrogen refuelling station must be compliant with requirements stated in different standards which require specialized sampling device and personnel to operate it. Currently, different strategies are implemented in different parts of the world and these strategies have already been used to perform 100s of hydrogen fuel sampling in USA, EU and Japan. However, these strategies have never been compared on a large systematic study. The purpose of this paper is to describe and compare the different strategies for sampling hydrogen at the nozzle and summarize the key aspects of all the existing hydrogen fuel sampling including discussion on material compatibility with the impurities that must be assessed. This review highlights the fact it is currently difficult to evaluate the impact or the difference these strategies would have on the hydrogen fuel quality assessment. Therefore, comparative sampling studies are required to evaluate the equiv-

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Sampling device
Fuel quality assessment

alence between the different sampling strategies. This is the first step to support the standardization of hydrogen fuel sampling and to identify future research and development area for hydrogen fuel sampling.

Contents

Introduction

Hydrogen-powered vehicles are one of the most efficient options for decarbonizing long-distance and heavy-duty vehicles [1]. Fuel cell electric vehicles (FCEVs) are fully carbon dioxide emission free, unlike other options such as biofuels, natural gas fuels and hybrids. A complete comparison of emissions even including emissions from the manufacturing process showed that FCEVs are also very competitive [2].

The development of FCEVs in our daily life requires the deployment of a refuelling infrastructure with hydrogen refuelling stations (HRSs) [3,4]. In 2020, the number of HRSs is above 140 in Europe [5] and 470 worldwide [6]. Regulatory requirements are implemented together with the infrastructure development. Hydrogen delivered at the HRSs must be compliant with requirements which are stated in different standards as for example the international standard ISO14687:2019 [7], the European standard EN17124:18 [8] or SAE standard J2719 [9]. These requirements have been established as a consensus based on extensive [10–12] yet ongoing research on the impact of contaminants on the fuel cell's ability to function properly. The most common method to monitor the quality of hydrogen at a HRS according to these standards is the so-called spot sampling which involves collecting a sample of gas at the nozzle in a sampling cylinder that is subsequently sent to a laboratory for analysis. The method requires specialized sampling equipment (often referred to as a sampling device), and personnel to operate it [13]. Due to the complexity of the measurement and the lack of online analysers to accurately determine the hydrogen fuel quality according to ISO 14687:2019, spot sampling is currently the only option to assess the hydrogen fuel compliance. The advantage of spot sampling is that laboratory analysis can be performed on the sample using a variety of analytical instruments. The disadvantages are that results are not obtained directly at the HRS and are representative of a single point in time. Sampling cylinders have insufficiently been tested at ISO 14687 threshold levels to guarantee that analysis results are representative for the hydrogen delivered at the HRS for all components [14].

Beyond the accuracy of the analytical method, taking a representative sample is of high importance for the hydrogen industry as important decisions (e.g. public access for refuelling) are based on the outcomes of the hydrogen quality assessment which includes the sampling procedure. This requires using appropriated sampling strategies including appropriate materials for the sampling devices and cylinders.

In this paper, strategies for sampling hydrogen at the nozzle of a HRS are defined as the list of components, requirements and procedures needed to safely install, fill and disconnect a cylinder and includes:

- The design (including the components) of the sampling device which is dependent upon the sampling method (for example, parallel or series).
- The sampling cylinder (one or two ended cylinder, size, material, treatment, valves).
- The different requirements in term of filling pressure, safety, connection fitting …
- The procedure to prepare the sampling cylinders before sampling (cleaning strategy).
- The procedure to purge the sampling device (for instance to remove air and water).
- The procedure to vent the device after sampling.

Currently, different strategies are implemented in different parts of the world and so far (i.e. ASTM D7607-17 in North America or the direct method in Japan), these strategies have been used to perform already 100s of hydrogen fuel sampling in USA [15], EU [16,17]and Japan. However, these strategies have never been compared on a large systematic study. Two bilateral comparisons have been recently performed in Europe (Hycora project [16,18]. It is of high importance to demonstrate that regardless of the strategy chosen, the outcomes of the hydrogen purity assessment are the same and that any bias due to the sampling strategy is avoided (i.e. the two scenarios where false results, negative or positive could occur must be avoided). A false positive (over-estimation) would be the case where the hydrogen is sufficiently pure but the sampling procedure itself contaminated the 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 sampling vessel.

The purpose of this paper is to describe and compare the different strategies for sampling hydrogen at the nozzle including summarizing all information available for the six parts described above for each strategy. Some information about some strategies can be found in at least two standards and in a recent study from Bacquart et al. [19] which described sampling procedures and purging for hydrogen samples taken both at low pressure (10–80 bar) and at the nozzle. The standard ASTM D7606-17 [20], describes in detail a sampling procedure for high-pressure hydrogen at stations operating at 350 or 700 bar with a method called “gas serial method”. The standard ISO19880–1:2020, annex K [21] describes summarily three methods: “parallel method”, “gas serial method” and “direct method”. However, the strategies “gas serial method” and “direct method” present technical similarities and in this paper, they have been grouped under the methods “gas serial method”. Other strategies have recently been developed by different organisations such as ENGIE, Air Liquide, Airborne Laboratories International and ZBT. Most of the strategies presented in this paper aim at filling a cylinder for offline analysis. However, recently developed strategies (ENGIE and Air Liquide) also include concepts to perform a partial onsite quality assessment (for example online analysis of water and oxygen).

The strategies using the “gas serial” method imply that hydrogen is filled in gas cylinder from the nozzle while the strategies using the “gas parallel” method include a tee-connection as component to parallelly fill the sampling cylinder and a vehicle tank.

Definition of the different sampling strategies

This paper will consider two different sampling strategies of hydrogen fuel for offline analysis called here “gas parallel” and

"gas serial". Both strategies concern sampling at the HRS nozzle.

"Gas serial": in these strategies, the sample is taken directly into a sampling cylinder. These sampling systems imply to manage the hydrogen fuel conditions and may require operating the HRS in service mode. The sampling system may also include a tank allowing to not override the protocol of the station (e.g. case of ENGIE method).

"Gas parallel": in these strategies, a tee-connection is used to parallelly fill the sampling cylinder and a FCEV or a receptacle (larger than the sampling cylinder). These strategies do not require to bypass the safety protocol of the station.

Strategies using the "gas serial" method"

At least four different strategies are based on the principle of the "gas serial method". One of these strategies is described in the standard ASTM D7606-7 [10] and two other strategies based on this principle have been developed by Air Liquide and ENGIE. The fourth strategy is the method currently used in Japan which is summarised in ISO19880-1, Annex K [21].

ASTM D7606-17 method

This method is currently used in the USA by companies conducting hydrogen fuel quality audits and is described in the standard ASTM D7606-17 [20]. 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 the Hydrogen Quality Sampling Apparatus (HQSA). The method is adaptable for stations delivering hydrogen fuel both at 350 and 700 bar. Airborne laboratories International have developed a commercial sampling device with Sulfinert® passivation (called NSP-7606) [22] compliant with ASTMD7606-17. It comes with 10-m 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.

Description of the system
The sampling is performed by connecting the HRS nozzle to the sampling device receptacle and venting of hydrogen to atmosphere through an exhaust stack. The components of the sampling device with receptacle (J2799 compliant), exhaust stack, quick connect fittings, pressure relief valves, valves and regulators are shown on Fig. 1 which is taken from the standard. The system has a high-pressure section (max 1000 bar) and a lower pressure section after the 1000 bar regulator allowing a maximum pressure of 140 bar (the pressure relief valve is set at 110 bar). The cylinder is located in the lower pressure section. The gas path in blue indicates the gas path during the filling procedure.

Sampling cylinder
The sampling cylinder is a 1-L stainless steel double-ended valve cylinder. The sampling cylinder and the valves should be passivated (internally coated with silicon) to minimize adsorption of sulphur species. During sampling, the cylinder is filled to a pressure of 69 bar and 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 estimate the amount of a contaminant in a hydrogen fuel system.

Information about the procedure
A cleaning procedure aiming at removing traces of moisture in the HQSA, sampling line and sampling cylinder is performed before sampling. Once the nozzle pressure has been regulated to 69 bar, the HQSA is cleaned by purging 1 kg of hydrogen fuel through the HQSA (the hydrogen flow rate is approximately 33.3 g/s). After sampling, a vent procedure is performed by opening the pressure release valve (14 on Fig. 1) before removal of the sampling cylinder. The hydrogen is then released through a check valve (16 on Fig. 1) and the ventilation assembly.

Air Liquide sampling device

To sample at the HRS nozzle, Air Liquide has developed a "gas serial" sampling system. The modular sampling device (Fig. 2) has two functions: it allows to measure the humidity onsite and to sample hydrogen for offline quality control of all other parameters.

Description of the system
The sampling is performed by connecting the HRS nozzle to the sampling device receptacle and by venting of hydrogen to atmosphere through a mobile vent. The device includes receptacle, quick connect fittings, pressure regulators, pressure relief valves, pressure gauge and mobile vents. The device is equipped with a parallel line to host a portable analyser (usually a moisture analyser) which can be used during the purge or the sampling phase (static or dynamic mode).

Sampling cylinder
The sampling cylinder is an aluminium double-ended valve 5-L cylinder (no specific treatment) with double-ended stainless-steel valves and is filled to 150 bar. Each cylinder undergoes a cleaning procedure at the laboratory. The cylinder is first emptied and flushed with nitrogen. The cylinder is then flushed with hydrogen (with a minimum of five pressurization and venting cycles) and then filled with residual hydrogen to around 5 bar. The system is suitable for 5-L cylinders with type E or DIN1 fittings. The use of other cylinders (volume or fittings) is possible if they possess intermediate fittings. Treatments of the cylinders are not prohibited.

Information about the procedure
Certain specifications must be followed to minimize safety risks (pressure or electrical): 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 and the flexible pipe connected to the sampling cylinder are equipped with an anti-whip cable, 3 – the flow path is equipped with a check valve connected to the portable vent system or the station's vent, 4 -each sampling cylinder 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, 5 - the device is connected to electric ground to avoid any electrostatic discharge.

Before sampling, an onsite cleaning procedure consisting of several pressurization – venting events (dynamic mode) or of a flush under a continuous flow (static mode) is performed onsite. Once the sampling cylinder is filled, the valves are closed, and the sampling device is vented through a vent pipeline.

Japanese approach

This method is currently used in Japan and is summarised in the standard ISO19880-1 Annex K [21]. In this standard, this method is considered as an alternative to gas serial and gas parallel methods but in practical terms, from the information available, the method is related to a "gas serial" method but uses a single-ended valve cylinder.

Description of the system
The sampling device consists of a receptacle (1), pressure regulator (2), safety release valves (3) and the sampling cylinder (4) as shown in Fig. 3 (from ISO19880-1). It also contains a pressure sensor and a temperature sensor positioned and operated in close proximity to the gas cylinder for safety reasons.

Sampling cylinder
The cylinder is made of manganese steel and the volume is typically 46.7 L [23]. It has polished inner surface (cylinder series. "SUMI-FINE"). The valves of the cylinders (type DSP21) are made of stainless steel. In the standard, a maximum pressure of 120 bars is specified (the cylinder itself has a max capacity pressure of 147 bar according to the manufacturer), it is only mentioned that the sampling is stopped when enough hydrogen has been sampled.

Information about the procedure
The sampling cylinder is cleaned with hydrogen (backfilling) and then kept under vacuum. The sampling cylinder is also purged onsite together with the sampling adapter through the vent system assembly. Typically, 1 kg of hydrogen is used for the purge.

ENGIE sampling device

To sample at the HRS nozzle, ENGIE has developed a device adaptable for stations delivering hydrogen fuel both at 350 and 700 bar and which also allows to perform online analysis of oxygen and water during a refuelling event. On the contrary to the other "gas serial methods, this method doesn't require the overriding of the safety protocol of the station.

Description of the system
The device (Fig. 4) consists of three lines; line A has a 55-L tank to simulate the presence of a FCEV vehicle, line B is dedicated to the online analysis of oxygen and water after pressure reduction (from 700 to 1 bar) and linc C is dedicated to the filling of the cylinder after pressure reduction (from 700 to 90 bar). All the lines are connected to the vent system. The device has three inlets, one for sampling at 350 bar stations, one for sampling at 700 bar stations and an auxiliary inlet for preparation and cleaning.

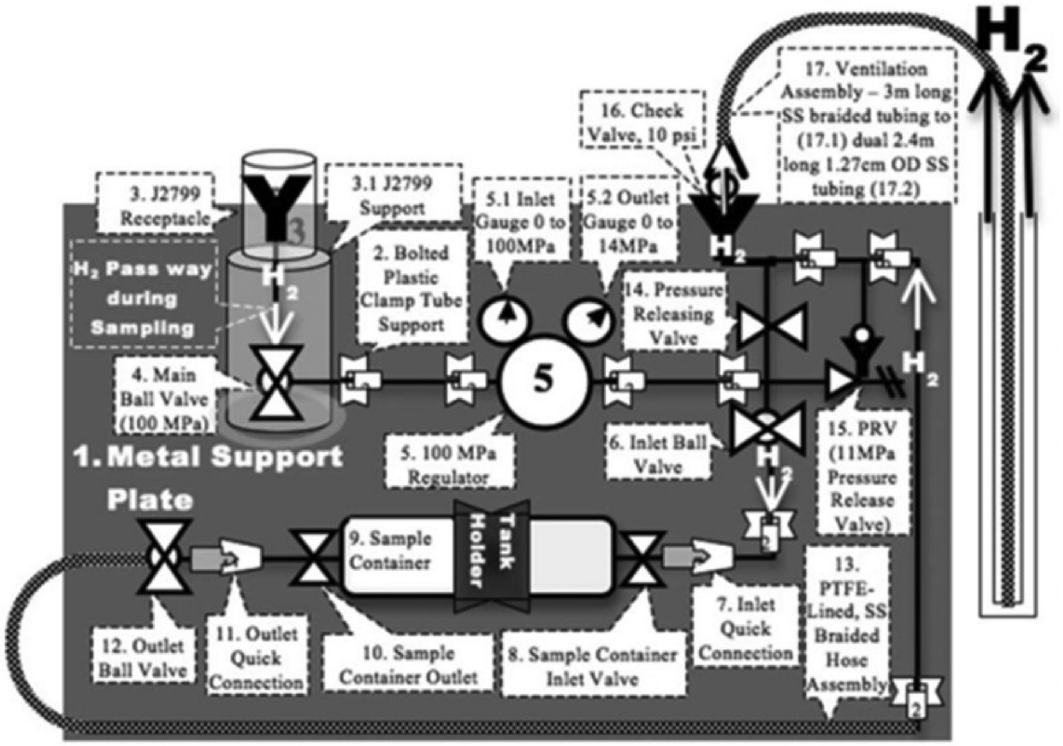

Fig. 1 – D7606-17 sampling device. Permission details.

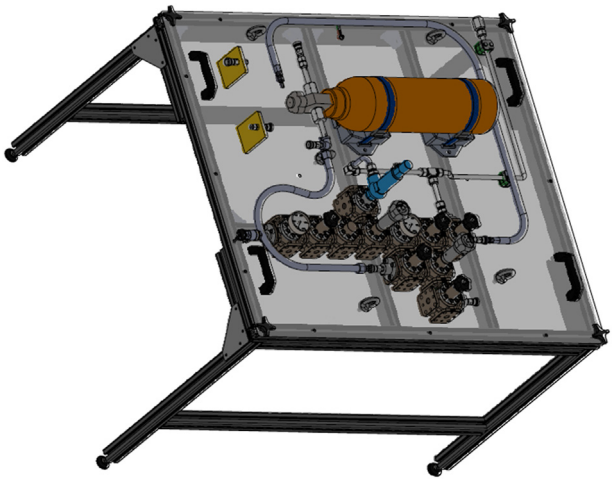

Fig. 2 – Air Liquide sampling system.

Sampling cylinder

Preferably, the sampling cylinder is a 1-L two ended valves coated stainless steel cylinder. Even if the ENGIE sampling device has been designed for the utilization of a two-ended valve cylinder of 1 L, it is quite flexible and other volumes of cylinders can be used (from 0.5 to 5 L). The device is fully compatible with cylinders equipped with other coatings or materials. Nevertheless, it is not adapted to sample with one-ended valve cylinders. The sampling cylinder is cleaned before sampling with nitrogen and a 500 mbar pressure is maintained in the cylinder.

Information about the procedure

During the onsite cleaning, the equivalence of 10 times to the volume of the cylinder is purged. After the vent, the device is flushed with nitrogen to remove the hydrogen before transportation.

Strategies with the "gas parallel" method

At least two different sampling strategies are based on the principle of the "gas parallel" method, one strategy using the Linde qualitizer and one strategy developed by ZBT. Sampling devices with the Linde qualitizer are used by several organisations who then adopt different sampling strategies (for example, slightly different types of cylinders with regards to the internal treatment or different protocols to prepare the cylinders and with or without methods to purge the sampling device).

Methods using the Linde qualitizer

The sampling is performed using a device called the Qualitizer manufactured by Linde. The filling of the cylinder is performed while a FCEV car is being refuelled.

Description of the system

The sampling device presented in Fig. 5 (from the standard ISO19880-1 [21] consists of a nozzle (4), a tee fitting (5), a vehicle and receptacle (6), a sampling cylinder with a pressure regulator and a pressure relief valve (3, 1, 2 respectively). The cylinder must have a DIN477 No1 valve to fit the pressure regulator (referred as number 2 in Fig. 5) of the Qualitizer device.

Sampling cylinder

The sampling cylinder is a one-ended valve 10-L cylinder in aluminum with standard DIN 477 No1 stainless steel valve. Linde uses aluminium cylinders with no specific treatment and SINTEF uses SPECTRA-SEAL® cylinders. The treatment consists of a proprietary process that renders the aluminum surface chemically inert. Additional processes convert the passivation layer into a surface with negligible adsorptive properties [24]. From a technical point of view, any cylinder suitable for hydrogen, equipped with DIN 477 No.1 valve and approved for the respective working pressure can be used.

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

Linde uses repeated pressure swing purges at 60 °C with nitrogen and then helium and subsequent evacuation.

The procedure followed by SINTEF in the HyCoRA project [25] has been to first evacuate the cylinders to 1 mbar, and then pressurize them to 10 bar using Ultra High Purity (UHP) hydrogen. This procedure is repeated three times before the cylinders are finally evacuated to 1 mbar prior to sampling use. The pressures (1 mbar and 10 bar) and number of cycles were chosen arbitrary and has not been validated at the laboratory but several sampling campaigns consisting of more than 40 samplings showed no evidence of carry-over from one sample to the next even if the cases where impurities were found in the hydrogen fuel above the thresholds in the standard ISO14687 [7].

NPL developed a seven steps method. The procedure is explained in detail in the MetroHyVe report A4.1.7 [26] 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 1.1×10^{-1} mbar or less) and the evacuation is subsequently done using the turbo pump (1×10^{-7} mbar). The outgassing of air, moisture and any remaining contaminants is monitored with 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.

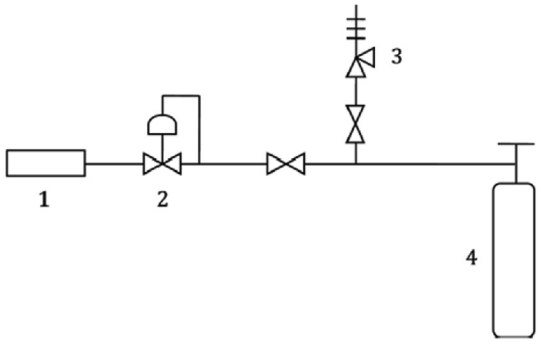

Fig. 3 – Sampling device used in Japan.

Information about the procedure

The filling of the cylinder is performed while a FCEV car is being refuelled. The tank of this car needs to be almost empty [19] so the refuelling process takes enough time so the pressure in the sampling cylinder reaches at least 50 bar. 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 3–5 min.

In ISO19880-1 Annex K, two procedures are proposed to purge the Qualitizer sampling device:

1) By Initiating a sampling but aborting within 15 s in order to isolate the test pulse and then depressurizing the sampling device with the bleed valve. The procedure is described in detail in Ref. [19].
2) By performing the operational procedure without connecting the sampling device to FCEV. The HRS safety will shut off hydrogen dispensing and depressurizes he bleed valve.

NPL procedure to purge the sampling device is explained in detail in the report A4.1.7 [26]. In this approach the sampling cylinders 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.

Hy-SaM sampling device

Within the German Hy-Lab project, ZBT and ZSW developed a sampling device called Hy-SaM (Fig. 6) which allows sampling according to the ISO19880-1 [21]and SAE J2601 [27] without overriding the refuelling protocol. It also offers the possibility of venting to atmosphere rather than using a FCEV.

Description of the system

The system is divided into three modules. Module 1 contains all parts for simultaneously sampling up to three cylinders (2.25 or 10 l) parallel to fuelling a FCEV. The complete sampling line of module 1 including quick connectors for the cylinders is coated (Sulfinert® also called Silconert® 2000). Module 2 is the mobile vent. Module 3 contains a buffer tank including the necessary safety components. By using module 2, sampling can be performed without refuelling a FCEV. Optionally, the vent lines (including safety relief valves) from modules 1 and 3 can be connected to module 2 or the HRS vent line. Also optional is the simultaneous sampling for particles.

Sampling cylinder

The sampling system can accommodate Spectra-seal treated 10 l aluminium cylinders with DIN 477 N.1 valve outlet or 2.25 l double-ended stainless-steel cylinders with internal coating (Sulfinert®). For connection to the sampling device, both cylinder types have quick connectors. All valves and connectors ae coated (Sulfinert®). The cylinders are usually filled to about 90 bar. Cylinders are conditioned by evacuation down to 10^{-7} mbar. The cylinders can be used evacuated or are pressurized with e.g. 300 mbar hydrogen (quality 9.0 which is obtained by when H_2 (5.0) passes through a palladium membrane purifier).

Information about the procedure

The nozzle of the HRS is connected to the receptacle of module 1. In case of sampling in parallel to a refuelling (without module 3), the module 1 nozzle is connected to the FCEX. Flushing of the hydrogen line is done by using the overpressure of an aborted refuelling and with the slight overpressure of the cylinder.

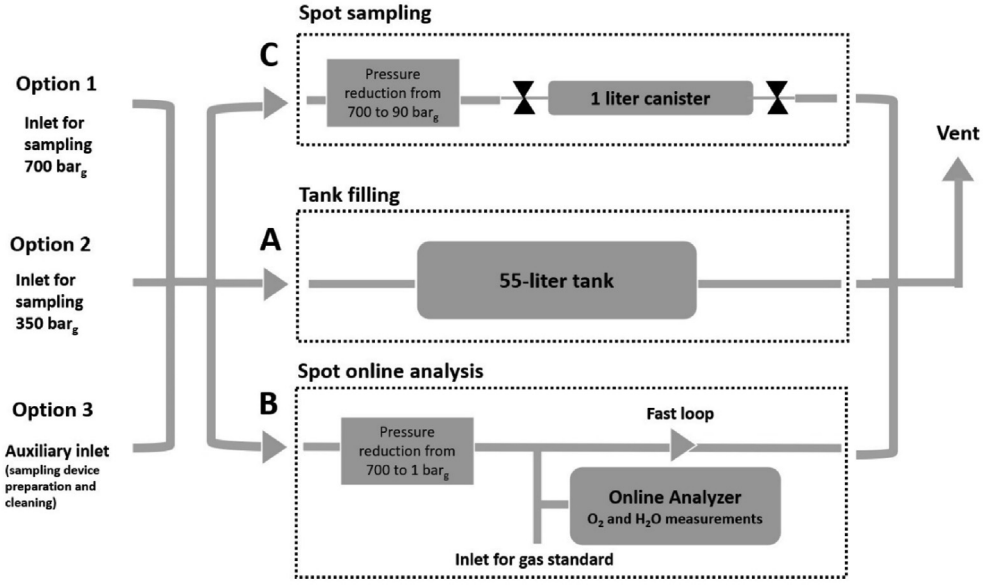

Fig. 4 – ENGIE sampling device.

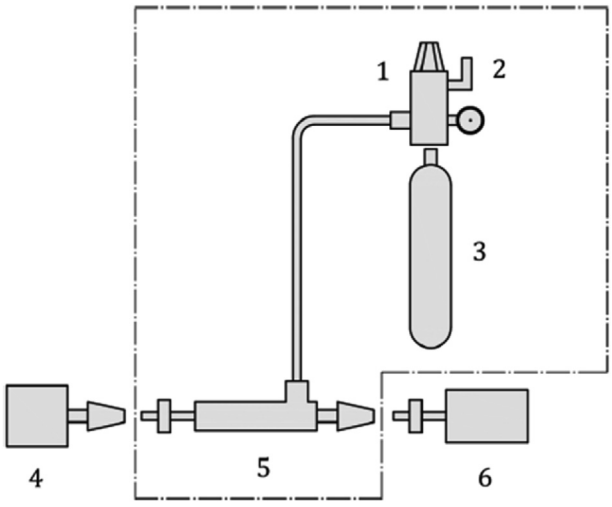

Fig. 5 – "Gas parallel" sampling device from ISO19880-1.

Discussion

The discussion will present the different issue related to the representativity of the hydrogen fuel sampling with regards to chemical composition (false positive and negative), then a summary of the different sampling strategies will be presented and the different parameters affecting the sampling discussed (sampling material behaviour, sampling cylinder, procedure). Finally, discussions about the safety of the sampling strategy, validation of the system and future online monitoring will bring a different perspective to the sampling strategy comparison.

Representativeness of the sample collected

The main purpose of all sampling strategies is to collect a sample of hydrogen that is representative of the hydrogen fuel composition dispensed at the station. This requires that no chemical compounds are added (false positive) nor removed (false negative) from the hydrogen fuel during the sampling.

False positive or contamination of the sample

Addition of compounds during the sampling can occur if the cylinder already contains impurities. It can be air and water if the cylinder or the sampling system has not been properly purged but also contaminants originating from previous utilizations of the cylinder if it has not been properly cleaned. The effectiveness of the procedure chosen to prepare the cylinders as well as the procedure to purge the sampling device before the sampling is of high importance and needs to be demonstrated.

All the sampling strategies mentioned in this study include a step for preparation of the cylinders before sampling. Therefore, it is expected that contamination from previous use of the sampling cylinders should not occur. However, there is no published study available on this carry-over effect, it is then important to log information about each sampling cylinder history. The purging procedure of the sampling device is also important to avoid false positives.

False negative of contaminant disappearing from the gas phase of the sample

Loss of chemical compounds from the gas phase during the sampling can occur if species present in the hydrogen fuel are adsorbed, absorbed or react for example by adsorption onto the wall of the cylinder or onto the sampling lines leading to the cylinder.

Materials are more or less prone to absorbing reactive compounds such as sulphur compounds, ammonia, formaldehyde, formic acid onto their surfaces. This problem is highly relevant for hydrogen fuel sampling as sulphur and other active compounds need to be quantified at trace levels (as low as 4 nmol/mol for sulphur). Therefore a defect of materials may hinder few nmol/mol of reactive compounds. It can be expected that many parameters such as the number of components of the sampling device, the function of the components used (for instance pressure reduction), the pressure, the temperature, the materials chosen may have an impact of the amount fraction of reactive compounds in the hydrogen fuel and in consequence to the representativeness of the sample collected.

It is worth noting that the different strategies presented here used different types of cylinders (stainless steel or aluminum, treated or untreated) and sampling devices with different components such as regulators, relief valves, presence ("parallel method") or absence ("gas serial method") of tee-connection. Some of the sampling devices have many components such as the ASTM D7606-17 method. The materials used are mainly stainless steel for the sampling device and aluminium or stainless steel for the cylinder. It is critical to assess each sampling strategy to understand the likelihood of false positive and false negative occurrence for each of them.

Summary of the different sampling system for hydrogen fuel quality art HRS

Table 1 presents the key aspects of all the existing hydrogen fuel sampling system. From the table, it is clear that there are difference and similarities between the approaches.

- All the approaches use sampling systems in stainless steel however it is not always clear if specific treatments are applied to the sampling systems. Additional components as pressure regulators, pressure gauges have not been sufficiently described to determine their potential influence on the amount fraction of the reactive species.
- All strategies imply a cleaning procedure of the cylinders and a sampling procedure involving purging to avoid false positive contamination.
- The sampling systems are using a large variety of gas cylinders. It is often not specified what is the rationale behind the cylinder's selection.

Sampling device - material behaviour

The sampling devices are mainly made of stainless-steel components. However, there are various types of stainless-steel (i.e. SS316, SS304) and different treatments (i.e.

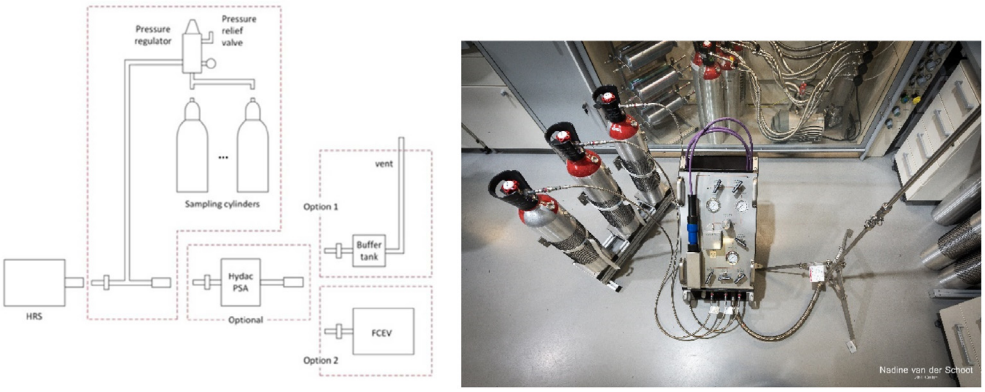

Fig. 6 – Hy-SaM sampling device.

electropolished, passivated Sulfinert®, silconert 1000) that make difficult to predict the actual behaviour of contaminants only based on the material.

Moreover, the different sampling system presented in this study has additional components (i.e. pressure regulator, pressure relief valves, pressure gauge), these compounds may have additional parts (sealent, gaskets, movable part) made of other materials which may have an impact on the reactive compounds. It is worth noticing that two systems for "gas serial" and "gas parallel" are currently Sulfinert® passivated: NSP 7606 and Hy-SaM. The comparison with untreated systems would be interesting to evaluate the criticality of the treatement. There is limited literature on the interaction of reactive compounds at nmol/mol level with materials. There are currently no easy ways to assess the performance of a sampling device regarding the representativeness of the sample collected.

The best way would be to build an experimental facility simulating a HRS (and including a nozzle) where hydrogen fuel could be contaminated by known fraction amounts of species including reactive species. Another possibility would be to use several sampling devices with defined sampling strategies at the same HRS and then compare the results of the analyses of the hydrogen fuel collected with different sampling strategies. However, if results differ from each other, it may be proven difficult to find the causes leading to these discrepancies as the composition of the hydrogen fuel is unknown. Finally, if reliable online instruments are used at the stations, the analysis report obtained while sampling with a defined strategy can be compared to the online measurements. However, as the online instruments are most likely not installed at the nozzle, once again, if discrepancies are observed, they cannot only be attributed to the sampling strategies.

Sampling cylinder – material behaviour

There are three main types of cylinders in use for hydrogen fuel sampling; aluminium, stainless steel and manganese steel.

By contact with air, aluminium surfaces [28] are passivated due to the development of an oxide layer and inertness can be improved by increasing the thickness of this oxide layer. However, aluminium oxide has an inherent, honeycomb like structure. Most of the reactions that take place on the internal surface of an aluminium cylinder are not direct reactions with the aluminium (oxide) surface, they are cavity enhanced reactions catalysed by the aluminium oxide structure. Reactive compounds are absorbed onto stainless steel through chemisorption. The addition of manganese into the steel improves strength and corrosion resistance of the alloy however no study has yet investigated its effect on contaminant stability.

Additionally to the cylinder type, there are several types of passivations or surface treatments existing: polishing or electropolishing of the internal surface (chemical or mechanical treatment), coating or passivation using inert silica layer (e.g. Sulfinert®), carboxylane coating (e.g. SilcoTek Dursan) [29] However chemical passivation or coating treatment tend not to be feasible for each cylinder type: Sulfinert® passivation can only be applied to stainless steel cylinder and can't be applied to aluminium cylinder due to material specification and safety. Other treatment as SPECTRA-SEAL (BOC) or Performax (Effectech) have been applied only to aluminum cylinder [29].

Some information about the impact on the material selection for the sampling cylinder on the representativeness of the sample collected can be found in literature, rarely in hydrogen matrix, but mainly in air or nitrogen. It can anyway provide information if stability when using different types of cylinder or internal cylinder passivation were observed. Satar et al. [30] did not observed significant difference in water amount fraction in nitrogen in various materials and treatment (including Sulfinert®®, aluminium or steel). Several compounds as helium, nitrogen, argon are almost considered as inert and no unstability is expected in any gas cylinder type. However, there is a lack of literature demonstrating it in hydrogen matrix. One recent study demonstrated stability of argon, nitrogen, helium, methane, ethane and carbon dioxide but only in SPECTRA-SEAL (BOC) and SGS (Luxfer) aluminium cylinders [31]. It is currently possible to buy these compounds in hydrogen gas cylinder through gas supplier (i.e. Air Liquide or Linde) with stability of 1 year minimum.

Total hydrocarbons cover a wide range of molecules from light linear hydrocarbon chains (e.g. ethane, butane) to long and heavy compounds (e.g. toluene, naphthalene) or highly polar compounds (e.g. ethanol, methanol) exhibiting different behaviour in gas phase. Therefore, it is important to

Table 1 – Sampling strategies characteristics.

	Gas serial				Gas parallel	
	Air Liquide	ASTM D7606:17	Gas direct	Engie Device	Linde qualitizer	Hy-SaM
Equipment (sampling devicerowhead	Quick connect fittings, modules with pressure regulators and manometers, mobile vents and allows for 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-L	Two-ended valve cylinder of 0.5 –2 L	One-ended valve cylinder of 47 L	Two-ended valve cylinder of 1 L	One-ended valve cylinder of 10 L	One-ended valve cylinder of 2.25-L or 10-L
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® coated
Requirements						
	Air Liquide	ASTM D7606:17	Gas direct	Engie Device	Linde qualitizer	Hy-SaM
HRS override	manual operation	yes	yes	no	no	no/yes
Filling pressure	~150 bar	69 bar	max 120 bar	90 bar	90–130 bar	~90 bar
Sampling duration	A) < 1 min/cylinder B) ~ 30min/installation	<1 min/cylinder		<3 min	<3 min	2–5 min
Maximum rated pressure	200 bar		147 bar	100 bar	160 bar	150 bar
Connection fitting	Quick connect fitting	Quick connect fitting	–	Quick connect fitting	Quick connect fitting	Quick connect fitting
Venting	Yes (mobile or HRS)	yes	yes		no (FCEV)	yes/no (FCEV)
Preparation procedures						
Cylinder Cleaning procedure (lab)	Standard cleaning procedure (on site) Several compression decompression Initial cleaning procedure for each new sampling cylinder or for those from a		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	previous sampling with an excessive amount of	Together with the sampling device	Together with the sampling device	Together with the sampling device	no	no
Procedure to purge the sampling devices	impurities (lab) 1) Emptying 2) Steaming with N2 3) Rinsing with H2 (minimum 5 cycles) 4) Filling with H2 residual (pressure ~ 5 bar)	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	By initiating a sampling, aborting, depressurizing the system and depressurizing the cylinders

investigate more than one type of hydrocarbons to ensure that the cylinder type is fit for purpose.

The stability of carbon monoxide at 100 nmol/mol amount fraction was studied in aluminium cylinder (untreated, SPECTRA-SEAL and SGS) [31,32], even if SPECTRA-SEAL and SGS aluminium cylinder showed a good stability, some issues were observed in untreated aluminium cylinder over long period of time (2 years). Considering the short duration between sampling and analysis, this type of untreated aluminum cylinder can be considered acceptable however it is not the best option to consider.

For very low amount fractions of reactive contaminants, like those specified in ISO 14687, there are very few studies on stability in different cylinders due to the complexity of preparing such gas mixtures. For hydrogen sulphide, stability in different cylinders have been the subject of several studies (however rarely in hydrogen matrices). Most of the studies on hydrogen sulphide tend to show that some kind of treatment of stainless steel or aluminium cylinders is required. For example, a study showed that hydrogen sulphide at a concentration of 17 nmol/mol [33] was totally lost after a 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 Sulfinert® coated cylinders. Another study has shown that 1.5 nmol/mol of hydrogen sulphide in air remained stable in Sulfinert® treated canisters [34]. Few stability results could be found for hydrogen sulphide at low nmol/mol in hydrogen matrix in aluminium cylinders. These studies pointed out a decay at concentration of 7–40 nmol/mol in aluminium cylinder with SPECTRA-SEAL treatment [31,32]. However, concentration of 5–15 nmol/mol was stable over few months in aluminium Superior gas stability - SGS cylinder [31]. The stability of hydrogen sulphide at 500 nmol/mol in synthetic air has been studied in different types of alumimiun cylinders [16] ("A": aluminium SGS cylinders, "B": basic alumimium alloy cylinders and AW: acid washed cylinders), for each type of cylinders, several cylinders were tested. Fast decay was observed in AW cylinders (total loss after 2 days) and in "B" cylinders (total loss after 10 days in most cylinders tested) while hydrogen sulphide concentration remained more stable in "A" cylinders. However even in these cylinders, a certain loss (up to 20% for one cylinder) is observed mostly at the beginning of the tests. Similar to the total hydrocarbons, total sulphur requires to investigate more than one sulphur molecule as dimethyl-sulphide (DMS). Recent study from the Korea Research Institute of Standards and Science (KRISS) achieved to 0.5–7.0 nmol/mol of DMS in nitrogen stable for at least a year in aluminum cylinder treated with Experis treatment (Air Products) [35]. Similarly, to total hydrocarbons, it is important to investigate more than sulphur compounds to ensure that the cylinder type is fit for purpose.

Other reactive species such as formic acid or formaldehyde have not been studied to the same extent as hydrogen sulphide and the implication of the sampling of a gas potentially containing several reactive species at trace levels have rarely been studied. Formaldehyde in hydrogen has been studied at 10 μmol/mol in aluminum SPECTRA-SEAL cylinder and has showed decay over time [36]. The authors suggested that decay was strongly dependent on the SPECTRA-SEAL cylinder itself. Stability issues are expected in hydrogen independently on the passivation treatment used due to the reaction with hydrogen as the surface of the cylinders was suspected to act as catalyst [37]. Other cylinder pre-treatments (Stainless steel with Sulfinert® passivation and aluminium with performax) are reported to show a better stability than aluminium cylinder with SPECTRA-SEAL. These cylinder types are reported to achieve a stability of 80% over 1 month at 1 μmol/mol formaldehyde in hydrogen [37]. A study [38] in nitrogen matrix demonstrated that Aculife VIII (Scott Specialty Gases) shows good stability down to 500 nmol/mol of formaldehyde.

Recent study showed instability of low amount fraction of formaldehyde in aluminium cylinder (SPECTRA-SEAL and SGS) in less than 24 h [31]. In the same study, formic acid was proven stable in SPECTRA-SEAL aluminium cylinder at approximately 400 nmol/mol while significant instability was observed in aluminium SGS for similar concentration over a short period. Other reports mentioned that formic acid is stable in aluminium cylinder at amount fraction from 10 to 100 μmol/mol in hydrogen for 1–5 years' time however it has been reported to be more challenging at nmol/mol amount fraction [37].

Ammonia has been studied in nitrogen matrix at amount fraction 10–100 μmol/mol and good stability was observed for stainless steel Sulfinert® coated cylinders for which no losses were observed. Relatively good performance was also obtained for SPECTRA-SEAL cylinders (BOC) and cylinders from Takachiho [39]. Recent study showed instability of low amount fraction of ammonia (~200 nmol/mol) in aluminium cylinder (SPECTRA-SEAL and SGS) in less than 24 h [31].

For HCl at approximately 400 nmol/mol amount fraction, only one cylinder type (aluminium Acculife IV) has been tested and the results showed that the measurement stabilization is slow with measured value significantly below the expected value [29]. Regarding halogenated species, it may be impossible to ensure that all chemical compounds are tested for their stability in gas cylinder. It may require extrapolating stability from few halogenated compounds (i.e. dichloromethane, chloroform, tetrachloroethylene, 1,2,3,4-$C_4Cl_4F_6$, dichlorobenzene, dichlorohexafluoro-2-butene). A recent study on dichloromethane showed this compound was stable in both SPECTRA-SEAL and SGS aluminium cylinders at approximately 50 nmol/mol over the period of a few months [31].

A recent study [31] demonstrated water was stable at around 5 μmol/mol in SPECTRA-SEAL and SGS cylinders for a few months, however, the same study mentioned that decay of any oxygen that could be present in the cylinder by reaction with the matrix hydrogen could cause instability of water. The study also showed that oxygen could be kept stable in both SPECTRA-SEAL and SGS cylinder for a few months but noted that differences had been seen in stability of oxygen between cylinders of the same internal passivation treatment.

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.

Validation of sampling Strategy

The comparison and validation of sampling strategies based on bilateral sampling and analysis is an important part of a method validation. Several activities to compare sampling strategies are ongoing in European projects. HYDRAITE project organises a bilateral comparison between HySaM sampling device and Qualitizer procedure in 2021 at a hydrogen refuelling station to evaluate any agreement or disagreement between the two strategies.

The strategies with the Qualitizer and Air Liquide sampler were compared at a HRS [19]. This study with the first bilateral comparison of two sampling systems emphasised that all contaminants were found to be below limit of detection. The two sampling methodologies agreed except on nitrogen amount fraction however it was suspected to be due to the hydrogen fuel at the HRS. As the HRS was previously in maintenance mode, it may be possible that the nitrogen amount fraction was linked to HRS infrastructure purging. Therefore, it is difficult to determine if there was any false negative effect due to the sampling system material or procedure.

Comparing sampling strategies at a HRS is therefore important to evaluate potential false positive however, studies using contaminated hydrogen would also be important if technically possible.

A recent campaign on 28 European HRS showed that most of the HRS are free of contaminants [18]. However, the study highlighted some limitations of the current quality control tools available for hydrogen fuel quality (lack of reference materials, standardized methods or inter-laboratory comparisons). Moreover, the limitations due to material compatibility can lead to false-negative results. If no contaminants are present in the hydrogen, the validation exercise will mainly assess the presence of false positive. The validation of the sampling strategy for all the compounds including reactive compounds at low amount fraction may be difficult to scientifically validate due to their absence in the fuel. Therefore, the development of alternative validation strategy involving synthetically contaminated fuel will be beneficial to assess the false negative or the impact of material on the fuel composition.

Sampling strategy and representativity of hydrogen

HRS have different designs that may involve several storage banks and different compression methods (for instance mechanical compressors or metal hydride compressors [40]). The two sampling approaches may differ regarding the representativeness of the sample collected It is therefore important that the sampling operator has an understanding of the HRS design to determine what would be the most relevant approach.

The parallel sampling follows the refuelling protocol and will therefore collect a fraction of the hydrogen fuel representative of the whole process at the HRS. This sampling then closely represents the actual hydrogen fuel received by the FCEV. However, it represents the situation of all the storage banks at the HRS so no information is obtained for one specific storage bank.

The serial sampling requires the station to be set in maintenance mode and the volume of gas sampled is lower due to the cylinder volume and its pressure rating. Therefore, hydrogen from only one storage bank may be sampled. It is important for the sampling operator to understand this specific feature as it may require multiple samplings if there are multiple storage banks (involving different processes as compression). The serial sampling will however allow to clearly evaluate the hydrogen fuel quality from this particular storage bank.

Advantages/disadvantages offline methods against online methods

Other aspects to consider are the time and the costs aspects. Once the sample of hydrogen has been collected, it must first be transported to the analysis laboratory following rules that are stringent due to hydrogen itself and then analysed before any conclusion can be drawn regarding the quality of the fuel dispensed. These two steps are time consuming and costly. Depending on the location of the HRS station and the location of the analysis laboratory, the hydrogen purity assessment report can be delivered in the best-case scenario after a few workdays and up to after a month or so in the worst-case scenario.

Currently, the cost to analyse one sample of hydrogen is evaluated to be between €6000 to €11,000 depending on the number of samples analysed at the same occasion. To the cost of analysis, the cost for sampling evaluated to be around €4000 needs to be added [41].

Once the results are known, the data interpretation should be a collaborative process between the HRS, the analysis laboratory and the personnel having performed the sampling, mostly if critical results are reported. For example, it will require investigating if the species found above thresholds originate from the hydrogen fuel itself or from one part of the sampling strategy, especially in the cases where oxygen, nitrogen and/or water are found. If online measurements of oxygen and water were to be performed at the station, this issue could be prevented. To this purpose, some of the sampling strategies presented here have included online analysers (Air Liquide method and ENGIE method). This feature also presents the advantage to directly give information on hydrogen fuel quality with regards to these species leading to immediate decisions to be taken (for instance shut down). However, it is not yet probable that all species can be monitored online due both to the lack of instruments; no instrument can so far monitor all the gaseous species at the required levels [42,43] and the high costs of instruments if all species were to be monitored online. Therefore, reliable sampling strategies for offline monitoring of the hydrogen fuel quality remain essential for the hydrogen industry.

Online monitoring at the HRS for a selection of species can be strategically implemented. For example, it can have the goal to target species with probability of presence “frequent” and “possible” [44,45] for the relevant hydrogen production

Table 2 – Cylinder suitability for a time period of 4 months.

	Stainless steel				aluminium									
	Untreated		Sulfinert®		Untreated		Aculife VII		Performax		SPECTRA-SEAL		Untreated SGS	
	a	b	a	b	a	b	a	b	a	b	a	b	a	b
C_2H_6	X	X	X	X	X	X	X	X	X	X	S	S	S	S
He	X	X	X	X	X	X	X	X	X	X	S	S	S	S
N_2	X	X	X	X	X	X	X	X	X	X	S	S	S	S
Ar	X	X	X	X	X	X	X	X	X	X	S	S	S	S
CO_2	X	X	X	X	X	X	X	X	X	X	S	S	S	S
CO	i.d.	S	i.d.	S	S	S	i.d.	i.d.	i.d.	i.d.	S	S	S	S
H_2S	i.d.	I/S	X.	S	i.d.	I	i.d.	I	i.d.	i.d.	I	I	S	i.d.
HCl	i.d.	i.d.	i.d.	I	i.d.	i.d.	i.d.	I	i.d.	i.d.	i.d.	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	I	I	i.d.
CH_2OH	i.d.	i.d.	i.d.	i.d.	i.d.	X.	i.d.	i.d.	i.d.	i.d.	S	S	I	i.d.
NH_3	i.d.	i.d.	i.d.	X	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	I	X	I	i.d.
O_2	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	S[a]	S[a]	S[a]	S[a]
H_2O	i.d.	i.d.	X[b]	X[b]	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	S[b]	S[b]	S[b]	S[b]

a: at ISO14687:2019 threshold.
b: at Higher concentrations (i.e. 50 times ISO14687).
X: should be suitable.
S: suitability demonstrated (* more than 80% stability over at least a month).
I: Issues were found (ex. of issues: need careful selection of the cylinder, initial loss …).
i.d.: Insufficient data.
[a] Oxygen stability seems to vary between cylinders of same internal treatment.
[b] Oxygen reactivity may affect the amount fraction of water through the reaction in hydrogen matrix.

method(s); CO and N_2 for steam methane reforming with PSA, and O_2 for chlor-alkali process) or to identify leaks and/or to control that the station has been properly purged after maintenance (by monitoring H_2O and O_2).

Safety of the sampling strategy

It is critical that the components of the sampling device for hydrogen fuel sampling at the HRS nozzle comply with local and international regulations. They should be operated by trained staff and follow regular maintenances 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 safely perform hydrogen venting at HRS during a sampling event. Depending on the device used, the quantity of hydrogen to be vented differs significantly. Moreover, some of the strategies already imply venting at the beginning of the sampling strategy to purge the sampling device; for instance the HQSA in the ASTM D7607 method is cleaned by purging 1 kg of hydrogen fuel through the HQSA. As hydrogen's flammability range is very wide, with a lower explosive limit (LEL) of about 4% and an upper explosive limit (UEL) of about 75%, hydrogen from vents and safety relief equipment shall be piped outdoors to a safe location where they do not generate a hazard for persons or neighbouring structures, away from personnel areas, electrical lines and other ignition sources, air intakes, building openings and overhangs [25]. Moreover, hydrogen refuelling stations are regulated environment with ATEX zone. The venting location, volume or flow needs to be agreed beforehand with the operators if a mobile vent facility is required. All systems have pressure relief valves, these safety valves may require to be connected to a safe vent. Otherwise, the hydrogen released in the 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 to allow all sampling equipment to be compatible to the HRS safety vent.

Conclusion

This study describes different sampling strategies to safely and representatively sample hydrogen at the nozzle of a HRS. Strategies consist of the choice of components for the sampling device inclusive the sampling cylinder, the design of the sampling device, the requirements in terms of filling pressure, safety, connection and fitting, the procedure to prepare the sampling cylinders before sampling, the procedure to purge the sampling device and the procedure to vent the device after sampling.

The strategies using the “gas serial” method imply that hydrogen is filled in gas serial from the nozzle in a sampling cylinder/and may require a tank) while the strategies using the “gas parallel” method include as component a tee-connection to parallelly fill the sampling cylinder and a car or a tank. The main purpose of all sampling strategies is to collect a sample of hydrogen that reflects the hydrogen dispensed at the station.

As materials are prone to absorbing reactive compounds onto their surfaces, it can be expected that many parameters such as the number of components of the sampling device, the function of the components used, the pressure, the temperature and specially the materials chosen may have an impact of the representativeness of the sample collected. It is of high importance to demonstrate that regardless of the strategy chosen, the outcomes of the hydrogen purity assessment are the same.

As it can be seen in this study, strategies currently implemented used different types of cylinders (stainless steel, manganese steel or aluminum, treated or untreated) and sampling devices with different components. A recent development is to implement online monitoring for a selection of species as part of the sampling strategy. Due to the lack of evidence on compounds stability in sampling gas cylinder, it is currently very challenging to demonstrate the representativeness of the sample collected.

This review highlights the similarities and differences between current sampling strategies. From a hydrogen fuel perspective, it is currently difficult to evaluate the impact or the difference it would have on the hydrogen fuel quality analysis results. Therefore, comparative sampling studies are needed to support the standardization of hydrogen fuel sampling.

As highlighted in this review, the implementation of online analysers for a selection of species would be extremely valuable as part of the sampling strategy and to validate the representativeness of the sampling strategy.

Declaration of competing interest

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

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