



# METROLOGY for HYDROGEN VEHICLES 2

## Deliverable D6

*Good practice guide for hydrogen quality sampling procedures/methods at HRS nozzles (harmonised with USA and Japan)*

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**EMPIR**



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Good Practice Guide - Good practice guide for hydrogen quality sampling procedures/methods at HRS nozzles (harmonised with USA and Japan)	
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<p><b>Summary</b></p> <p>This good practice guide was written as part of activity 3.2 from the EMPIR Metrology for Hydrogen Vehicles 2 (MetroHyVe2) project. The three-year European project commenced on 1<sup>st</sup> 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 <a href="https://www.sintef.no/projectweb/metrohyve-2/">https://www.sintef.no/projectweb/metrohyve-2/</a>.</p>	
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## Introduction

At the end of 2022, the number of hydrogen refuelling stations (HRS) is above 250 in Europe and above 800 worldwide [1]. Regulatory requirements have to be implemented alongside the infrastructure development. The rapid growth of hydrogen infrastructure is driving rapid evolution and implementation of the regulatory requirements. One of these regulatory requirements is the hydrogen fuel quality.

Hydrogen delivered at the HRSs must be compliant with requirements which are stated in different standards as for example the international standard ISO14687:2019 [2], the European standard EN17124:18 [3] or SAE standard J2719 [4]. The most common method to determine the hydrogen fuel quality at an HRS according to these standards is the spot sampling. It requires collecting a sample of hydrogen fuel at the HRS nozzle in a sampling cylinder that is then sent to a laboratory for analysis. Even if online analysers have developed quickly, spot sampling is currently the only option to assess the hydrogen fuel compliance at HRS. The advantage of spot sampling is that analytical laboratory can perform the hydrogen fuel analysis using a variety of analytical instruments.

The spot sampling method requires to take a sample at the HRS nozzle in challenging conditions including temperature (i.e., down to -40 °C), pressure (i.e., 0 – 700 bar) and flow variation (i.e., 0 – 60 g/s). It requires specialized sampling equipment (often referred to as a sampling device), and personnel to operate it. Currently, different strategies are implemented in various parts of the world. For example, serial sampling strategy (i.e., ASTM D7606-17 [5]) is used in North America and parallel sampling (i.e., H2 Qualitizer) is often used in Europe. These strategies realised already 100s of hydrogen fuel sampling in USA [ref], EU [6] and Japan [ref]. It is critical to demonstrate that regardless of the strategy chosen, the outcomes of the hydrogen purity assessment are the same and that any bias is avoided due to the sampling strategy (i.e., false results, negative or positive).

Despite HRS samplings being widely deployed, these strategies have never been compared on a large systematic study. Only few bilateral comparisons were realised in Europe as part of HyCORA project [7]. Two key aspects of the sampling equipment are the sampling system including its operating method and the sampling cylinders. Sampling cylinders have insufficiently been assessed for compounds stability at ISO 14687 threshold levels. This study would guarantee that analysis results are representative of the hydrogen delivered at the HRS for all components [8]. The MetroHyVe 2 consortium is addressing the sampling container in a dedicated D5 "Good practice guide for handling of hydrogen fuel sampling containers (harmonised with USA and Japan and including preparation, delay for analysis, lifetime and transfer) at HRS nozzles".

This report and guidance focussed on the sampling procedures/methods at HRS nozzles. The objective is to provide new insights on the equivalence of sampling system at HRS. This report will complete the open access review published by the MetroHyVe 2 consortium and expand the current knowledge to support the development and deployment of new sampling equipment in EU and worldwide. Moreover, this good practice guide supports the harmonisation of hydrogen fuel sampling and future evolution of ISO 19880-9 through technical evidence and guidelines.

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. Reliable and representative sampling is a cornerstone of hydrogen fuel quality monitoring and the successful deployment of hydrogen fuel quality for vehicles.

## Review of sampling strategies

Currently, there is two different sampling strategies of hydrogen fuel for offline analysis called here “gas parallel” and “gas serial”. Both strategies are applicable to sampling at the HRS nozzle. The MetroHyVe 2 partners have realised a complete and open access state of the art review of hydrogen fuel sampling at HRS in the journal International Journal of Hydrogen Energy. The review offers a comprehensive and detailed information on the different sampling systems in operation [8]

“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). [8]

“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. [8]

Currently there is limited number of sampling system commercially available. Therefore, the only suitable option is to build or get build a bespoke sampling system. The number of hydrogen sampling system for HRS nozzle is small with less than 15 systems and even less design operating in Europe, North America, and Japan. The MetroHyVe 2 consortium was able to access most of the sampling systems worldwide. Three European parallel sampling strategies were used experimentally H2 Qualitizer (Linde, AT) owned by NPL and SINTEF, HySAM owned by ZBT and ENGIE sampling system (designed by ENGIE) owned by ENGIE. Three serial or direct sampling strategies were used experimentally direct sampling system (Iwatani, JP) owned by Iwatani Japan, Air Liquide sampling system (Air Liquide, FR) and Division of Measurement Standards (DMS) sampling system (supplier?) owned by California Department of Food and Agriculture - Division of Measurement Standards.

## Challenges

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 were realised in European projects as a bilateral comparison between HySaM and H2 Qualitizer sampling device [6-9]. The studied showed no significant disagreement between the two parallel strategies. The comparison of parallel and serial strategies was realised using the H2 Qualitizer and Air Liquide sampler at one HRS [10]. This study emphasised that all contaminants were 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 an HRS is therefore important to evaluate the equivalence between strategies. The realisation of a sampling intercomparison requires access to all the sampling equipment with trained staff, an HRS able to accommodate all the sampling system and their technical requirements (i.e., HRS manual override, FCEV or mock up tank). Moreover, the presence of contaminants is preferred to assess real variation between strategies. If no contaminants are present in the hydrogen, the validation exercise will mainly assess the presence of false positive.

The availability of the sampling equipment, the HRS site and access highlight the challenges to provide some new knowledge supporting the equivalence between sampling strategies.

## Sampling strategy equivalence

MetroHyVe 2 partners have developed or acquired bespoke sampling systems (i.e., Air Liquide sampling system, Engie sampling system, HySAM for ZBT, H2 Qualitizer for SINTEF and NPL). In other parts of the world, DMS has a sampling system following ASTM D7606-17 and IWATANI has a direct sampling system compliant with Japanese regulations (similar strategy as serial sampling).

The different strategies referenced previously may be suitable based on the technical requirement. The engineering body that will develop the sampling equipment will ensure its compliance with the refuelling stations requirements according to ISO 19880-1 and in the future with the requirements of ISO 19880-9.

However, it is important to verify that the different sampling strategy and device are equivalent, and the hydrogen gas sampled is equivalent and unbiased. Therefore, MetroHyVe 2 consortium realised three sampling intercomparisons. One analytical laboratory (i.e., NPL) performed all the analysis in repeatability condition to avoid any bias due to the analytical measurement.

### Equivalence between ASTM D7606-17 serial sampling and H2 Qualitizer parallel sampling approach

#### Strategy of the exercise

SINTEF (NO) and DMS (CDFA, US) realised a series of sampling at HRS in California (Aliso Viejo and Costa Mesa). The objective was to compare the two approaches in condition as close as possible to repeatability conditions. Therefore, DMS and SINTEF realised consecutive samplings at multiple HRSs using the two sampling systems operated by their sampling experts. The DMS sampling system is a serial sampling compliant with the ASTM D7606-17 standard. The sampling system has been used for large sampling campaign over the past years in California and is considered as the reference in US. The SINTEF sampling system is a parallel sampling system referred as the H2 Qualitizer. The H2 Qualitizer has been used in various EU projects (i.e., HYDRAITE, HyCORA) to realise hydrogen fuel sampling in Europe. Therefore, it has been established as an EU sampling reference.

#### Description of sampling system and the HRS

Back-to-back sampling of fuel were performed with EU and ASTM D7606 strategies at two HRS in Southern California with support from HRS operator First Element and Toyota Motor North America providing a vehicle for sampling with H2 Qualitizer. The sampling with H2 Qualitizer was realised first followed with DMS sampling in the two occasions.

#### *DMS sampling system – Serial sampling*

Standard practice for dispensed hydrogen fuel quality control is to collect a representative sample from the nozzle of the HRS. In the US, the methodology has been developed in ASTM D7606 Standard Practice for Sampling of high-Pressure Hydrogen and Related Fuel Cell Feed Gases. The sample was collected at reduced pressure through a sampling device that either vents to air or through connection to the HRS safety vent. A sampling cylinder open in both ends is used and extensive purge-though is performed before the sample is collected. The procedure requires the HRS to be put in manual mode.

#### *SINTEF sampling system – Parallel sampling*

In Europe, most of the hydrogen fuel quality control has been performed by using a commercial sampling adapter from Linde. “The Qualitizer” makes use of a T-piece between the HRS nozzle and the vehicle to bleed off a sample during a normal refueling. The sample is collected in a 10 L single-ended cylinder previously evacuated to low vacuum ( $< 10^{-7}$  mbar).

No venting or purging of hydrogen H2 Qualitizer was performed except from a small volume from depressurization of the adapter after use. The procedure does not require the HRS to be put in manual override.

## Results of the experimental comparison

### *Serial versus parallel sampling*

The results of analysis in Table below showed that the parallel and serial sampling agreed on most compounds except on oxygen and water. The parallel sampling showed higher value than the serial sampling for oxygen and water. The lack of purging in the H2 Qualitizer may be one reason for a slightly higher amount of water and oxygen.

The limit of detection of the analytical laboratory was not low enough to determine the correlation between oxygen level and air contamination. The nitrogen amount fraction would have been around 16  $\mu\text{mol/mol}$  in case of an air contamination which is below the laboratory limit of detection (LOD).

Table 1. Results of analysis from the hydrogen fuel sampling realised in the SU by SINTEF and DMS.

Constituent	ASTM Method	HRS 1			HRS 2		
		H2 Qualitizer - Parallel sampling	H2 Qualitizer – sample transferred into small canister	DMS - Serial sampling	H2 Qualitizer - Parallel sampling	H2 Qualitizer – sample transferred into small canister	DMS - Serial sampling
		amount fraction [ $\mu\text{mol/mol}$ ]					
Water	D7941	1.438	1.480	0.838	1.928	1.939	0.835
Total hydrocarbons - Methane	D7675	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
Methane	D7675	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
Oxygen	D7607	3.96	< 2	< 2	< 2	< 2	< 2
Helium	D7833	< 40	< 40	< 40	< 40	< 40	< 40
Argon	D7833	< 25	< 25	< 25	< 25	< 25	< 25
Nitrogen	D7833	< 25	< 25	< 25	< 25	< 25	< 25
Carbon dioxide	D7653	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Carbon monoxide	D7653	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08
Total sulfur compounds	D6228	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003
Formaldehyde	D7941	< 0.002	0.008	0.007	< 0.002	< 0.002	< 0.002
formic acid	D7653	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
ammonia	D7941	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004
Total halogenated compounds	D7892	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003

The comparison of ASTM D7606-17 serial sampling and H2 Qualitizer parallel sampling approach showed equivalence for all compounds except water amount fraction. The results suggested insufficient purging of the parallel sampling method. Additional purging of the H2 Qualitizer is feasible but often a challenge due to health and safety concerns on the hydrogen release in ATEX zone of the HRS.

The difference on the water amount fraction may be related to the sequence of sampling (H2 Qualitizer first then DMS sampling). It would be interesting to investigate the impact of the sampling sequence on the water amount fraction of the hydrogen fuel sampled. The HRS parameters (gas temperature, cooling) may be important in the evaluation of water amount fraction in hydrogen samples.

To ensure complete equivalence, good practice would be to realise at least one more purge on the H2 Qualitizer or parallel approach. It is possible if the purge is vented through a safe vent which is currently not available on the H2 Qualitizer.

Updating the H2 Qualitizer is therefore recommended to ensure the purge valve is ported to a safe vent. Any new parallel sampling system shall include ported purge valve to allow purging and avoid positive bias (i.e., high water amount fraction).

## Comparison of one serial and three parallel sampling systems in Europe

### Strategy of the exercise

The sampling was realised in condition as close as possible to repeatability conditions. The H2 fuel samplings were realised at ZBT HRS in Duisburg.

ZBTs HRS test station consists of three storage banks with a total hydrogen capacity of approximately 500 kg (stored at 200, 500 and 900 bar). The ZBT HRS is used in different research projects. After the research experiment, the hydrogen used in the fuelling tests is not released into the atmosphere but recycled back into the storage banks. Therefore, the ZBT HRS may have noticeable amount fraction of several compounds which is interesting for a sampling intercomparison. On the other hand, and due to the number of storages, it may lead to an inhomogeneous distribution of compounds between the individual storage banks.

Pre-cooling can be controlled from -40°C to ambient temperature, with a solid and plate heat exchanger available. Mass flows up to 120 g/s are possible. Refuelling can be done at 700 bar (LD) and 350 (500) bar HP. Possible refuelling protocols are: SAE J2601, MC formular, PHRYDE & "free" configurable.

All the H2 fuel sampling were realised consecutively without any external events in between. The order of sampling was ENGIE sampling system (ENGIE), H2 Qualitizer (NPL), Air Liquide serial sampling (Air Liquide), HySAM (ZBT) and a second ENGIE sampling to access repetition (starting and closing the sampling intercomparison).

### Description of sampling system and the HRS

#### *Air Liquide system*

The Air Liquide sampling device is a serial sampling device where sampling is performed to a 5 L aluminium cylinder with double-ended stainless-steel valves. The sample cylinder is prepared according to an Air Liquide procedure in order to ensure that it's not polluted, and that the analysis is representative of the customer's product. The cylinder contains a slight overpressure of pure hydrogen at the start of sampling. The HRS was set to provide 180 bar constant pressure and pre-cooled hydrogen to T20. The system was repeatedly (10 times) purged by hydrogen from the HRS through pressurization and venting before the procedure was repeated with purging through the sample cylinder (10 times). The sample cylinder was then filled to 150 bar. The sampling device has a valve port with pressure reduction for installation of an inline water analyzer. The indication of water content was used to ensure that the water content in the sampler was in line with customer specifications before the sample cylinder was filled.

#### *ENGIE system*

The Engie sampling device is a multi-purpose sampling device for 70 MPa, 35 MPa as well as functionality for online fuel quality control. ENGIE system has a 55 L composite tank simulating the presence of a FCEV. A dedicated sample line enables sampling with two 1 L double ended cylinders parallelly to the tank refueling. Another separate line incorporates a fast loop for online analysis with a AP2E Optical Feedback Cavity Enhanced Absorption Spectrometer (OFCEAS) to monitor oxygen and water (and give access to methane, H<sub>2</sub>S and CO<sub>2</sub> amounts).

The sampling device was connected to the HRS through the 70 MPa receptacle. The HRS was set to provide hydrogen at constant 20 MPa pressure with a T20 pre-cooling. The sampling device was



flushed repeatedly (10 times) with nitrogen and UHP hydrogen before sampling. Two 1 liter sample cylinders (stainless steel and Sulfinert® coating) were purged with nitrogen and prefilled with 1 bar UHP hydrogen before installation on the sampling device. The sampling device were purged with nitrogen after use to be transported (the device is PED certified).

The ENGIE device collected two samples first, and then two samples last of all sampling to check of consistency of sampling but also for possible variation in hydrogen quality over time.

#### HySAM system

The Hy-SAM adapter designed by ZBT and ZSW [8] is a parallel sampling strategy system. The system was detailed in the open access article from MetroHyVe 2 consortium [8]. It also offers the option of parallel sampling to up to three sample cylinders of size 2.25 or 10 L. The sampling time can be varied through adjusting the flow of sample (using a needle valve) to the cylinder(s). The system is completely passivated to prevent adsorption of impurities onto surfaces.

The system was purged on the high-pressure side by an aborted refuelling. With the sample cylinders pre-filled to 10 bar with ultra-high purity (UHP) hydrogen, purging of the low pressure side of the sampler was also performed. For this campaign, two 10 L aluminium spectra-seal lined cylinder with stainless steel valve were used. A 244 L tank was again used as sink.

#### H2 Qualitizer

The H2 Qualitiser system is a parallel sampling strategy system. The system was detailed in the open access article from MetroHyVe 2 consortium [8]. A small-bore high-pressure hose connects the tee to a 1034 bar Tescom reduction valve equipped with a safety relief valve and a manometer. The flow is throttled to fill the sample cylinder to around 10 MPa in the time it takes refuel a light duty vehicle. The sampling cylinder used was a 10 L aluminium spectra-seal lined cylinder with stainless steel valve. The sampling cylinder were previously prepared with a vacuum better than  $10^{-7}$  mbar.

The Linde Qualitizer sampling was performed by applying a normal fueling protocol. A 244 L Hexagon 70 MPA Type IV tank was used as sink instead of a FCEV. The system was purged through a bleed valve on the Tescom through the following steps: refuelling was aborted and the Qualitizer depressurized prior to sampling.

#### Sampling intercomparison experimental setup

The samplings were realised as close to real sampling conditions as possible, therefore the HRS station parameters were not set and the filling protocol SAE J2601 was followed for all the sampling event except for the Air Liquide serial sampling that required the refuelling station to be in maintenance mode. All the sampling were realised using T20 cooling prior to the sampling.

#### Results of the experimental comparison

##### HRS parameters evolution (temperature, filling rate and storage bank uses)

During the consecutive samplings, the HRS stations parameters were monitored. For each sampling, the SAE J2601 protocol was used, or the operators set the HRS parameters which is presented in the Table below.

##### Use of storage bank

As the HRS used for the study has seven storage banks, the use of the storage bank was interesting to monitor and compare between the different samplings. The table 1 and 2 summarised the use of the storage banks.

Table 2. Used storage banks and sampling conditions for the sampling intercomparison realised at ZBT refuelling station.

Participant	storage bank/Buffer tank						
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	Type of sampling	1	2	3	4	5	6	7	Average filling rate [g/s]	End pressure [bar]	Time [s]	SAE-J2601 conform	cooling (solid heat exchanger)
ENGIE Sampling 1	Parallel	58%	-	-	-	-	-	42%	3.9 ± 0.6	714	540	Yes	T20
H2 Qualitizer – sampling 1	Parallel	-	100%	-	-	-	-	-	14.3	738	174	Yes	T20
H2 Qualitizer – sampling 2	Parallel	40%	30%	-	-	-	29%	-	14.1 ± 1.0	738	170	Yes	T20
Air Liquide sampling system	Serial	-	-	100%	-	-	-	-	3.3	200	157	No	T20
HySAM	Parallel	27%	61%	-	-	-	12%	-	15.3 ± 2.2	738	278	Yes	T20
ENGIE Sampling 2	Parallel	50%	-	-	-	-	-	50%	3.95 ± 0.55	714	560	Yes	T20

The results are interesting as the different samplings even consecutive did not sample from the same combination of storage bank. More interestingly, the three parallel sampling which are meant to sample on parallel of a vehicle showed different storage bank used. Therefore, consecutive sampling as consecutive refuelling may not be filled by the same storage bank. The serial sampling was only sampling one of the storage banks. The results showed that two important aspects of the two sampling strategies regarding hydrogen storage:

- serial sampling sampled only one storage bank. If the HRS is operating using multiple storage banks, this sampling may miss some information related to other storage banks. The necessary assumption for serial sampling is the hydrogen quality is the same in all the storage banks.
- parallel sampling sampled only the storage bank used by the specific FCEV refuelled. It may not sample all the storage banks of the HRS that may be used to refill the consecutive drivers. It is important to understand how the filling protocol is operating and using the storage bank to ensure that the sampling represents more than the individual FCEV refilling events. The necessary assumption for parallel sampling is the storage banks of the HRS are either always used for the FCEV refuelling or that they are all equivalent quality. The results in Table 2 showed that despite using the SAE J2601 filling protocol, the three parallel sampling (HySAM and H2 Qualitizer) were not using the same storage bank nor the same proportion of them. Therefore, the knowledge of the storage bank architecture of the HRS is important to design a suitable sampling strategy (i.e., number of cylinders, specific filling protocol).

#### Filling rate variation

The filling rate diverged significantly between sampling system with the parallel sampling using FCEV (or equivalent) being around 14 – 16 g/s while the parallel system using a small tank being 3.9 – 4.0 g/s. It is interesting as this parallel system followed the SAE J2601 protocol but we filling flow were significantly different.

The serial sampling has a relatively slow filling rate of 3.3 g/s but the filling is completed within the same time as the parallel sampling using FCEV (or equivalent). The relatively slow filling was due to the sampling vessel size which is way smaller than a FCEV tank and get filled only to 150 – 200 bar.

#### Temperature variation

The variation of the flow rate and the temperature is presented in Figure

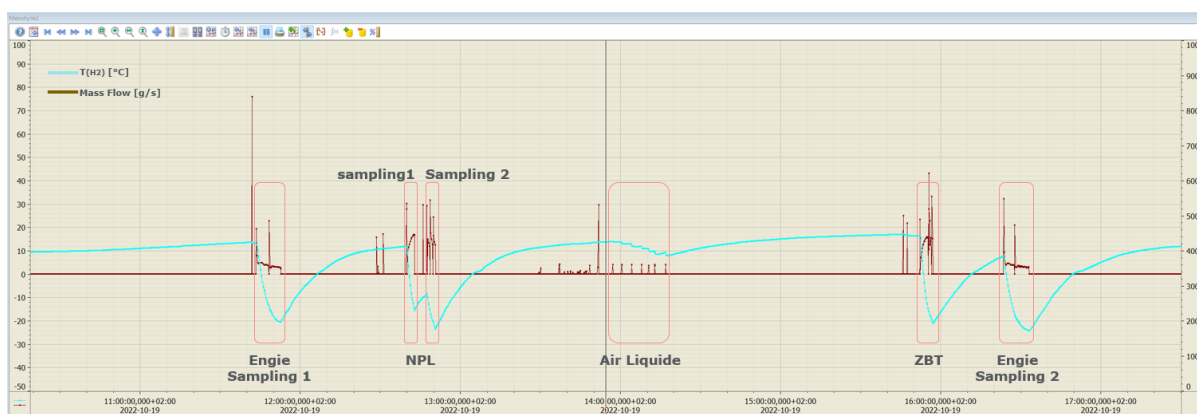


Figure 1. Temperature and mass flow variation during the sampling intercomparison realised at ZBT refuelling station. The blue curve presents the temperature variation, and the red curve presents the flow rate variation. The boxes represent the duration of the different sampling realised.

The temperature profile of the gas during the sampling is presented in Table 2. As the precooling was set at T20 for all the sampling experiment, the profile from the parallel sampling were similar (HySAM, ENGIE and H2 Qualitizer) with temperature decreasing as the sampling progress to temperature close to -20 °C. The slope for the parallel sampling was quite similar. It should be noticed that consecutive sampling influenced the temperature of the gas as the second NPL sampling realised much lower temperature than all other sampling.

In the case of the serial sampling, the gas temperature did not seem to decrease a lot. Sampling of the serial system (Air Liquide sampling system) was divided in 9 sub-samplings with long flushing-periods in between. The result is a very short contact time with the cooling unit. It would explain the relatively high temperature of the gas during the sampling.

The current sampling strategy using parallel or serial sampling showed different profile of filling rate, temperature, duration, and storage bank used. There are differences observed and assumptions that need to be made to ensure that the hydrogen fuel sampled is representative of the HRS.

In the case of a simple HRS (one storage bank or low pressure and high-pressure storage bank), the variation in the storage bank usage may not be a significant issue. However, in the case of a complex HRS (i.e., with substantial number of storage bank, feedstock), the strategy may be challenged to achieve a representative hydrogen fuel sample of the overall HRS.

### Results of analysis of gas samples

The results of analysis from the hydrogen fuel samples taken by the different sampling system were presented in the table below.

Table 3. Results of analysis of the hydrogen sampled by the four different sampling systems. Analyses were performed in repeatability conditions and covered ISO 14687 specification.

Component	ISO 14687:2019 Grade D ( $\mu\text{mol/mol}$ )	Measured amount fraction / ( $\mu\text{mol/mol}$ )					
		ENGIE Sampling 1	H2 Qualitizer sampling 1	H2 Qualitizer sampling 2	HySAM	Air Liquide serial sampling	ENGIE Sampling 2
Cylinder reference	-	ECH-1	D914172	D913273	D610586	AL8407	ECH-2
Nitrogen	300	$364 \pm 11$	$248 \pm 9$	$307 \pm 9$	$240 \pm 7$	$408 \pm 12$	$360 \pm 9$
Argon	300	$0.84 \pm 0.05$	$0.68 \pm 0.05$	$0.76 \pm 0.05$	$0.64 \pm 0.05$	$0.58 \pm 0.05$	$0.79 \pm 0.05$
Helium	300	$5.5 \pm 0.9$	$5.6 \pm 1.1$	$5.6 \pm 1.1$	$5.2 \pm 1.3$	$4.7 \pm 1.3$	$5.6 \pm 1.1$
Oxygen	5	$0.69 \pm 0.09$	$2.03 \pm 0.07$	$0.39 \pm 0.08$	$0.31 \pm 0.08$	< 0.3	$0.62 \pm 0.08$
Water	5	$6.76 \pm 0.34$	$13.3 \pm 0.8$	$1.82 \pm 0.11$	$5.60 \pm 0.33$	$20.2 \pm 1.2$	$4.45 \pm 0.23$
		$6.58 \pm 0.33$					$4.74 \pm 0.24$

Carbon dioxide	2	2.87 ± 0.28	1.42 ± 0.14	1.97 ± 0.19	1.32 ± 0.13	0.92 ± 0.09	2.45 ± 0.24
Methane	100	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Non-methane hydrocarbons <sup>(1)</sup>	2	0.071 ± 0.005	0.407 ± 0.017	0.058 ± 0.007	0.056 ± 0.007	0.065 ± 0.008	0.070 ± 0.008
Carbon monoxide	0.2	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015
Formic acid	0.2	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020
Ammonia	0.1	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015
Formaldehyde	0.2	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Total halogenated compounds <sup>(2)</sup>	0.05	< 0.018	< 0.018	< 0.020	< 0.018	< 0.019	< 0.018
Individual organo-halogenated compounds <sup>(3)</sup>	-	< 0.0017	< 0.0017	< 0.0019	< 0.0017	< 0.0018	< 0.0017
Total sulphur compounds <sup>(4)</sup>	0.004	< 0.0008	< 0.0008	< 0.0008	< 0.0008	< 0.0008	< 0.0008

The results of analysis from the four different sampling system did not show any presence of carbon monoxide, methane, formic acid, formaldehyde, ammonia, total sulphur compounds, halogenated compounds. The helium amount fractions were similar between all the sampling methods around 5 µmol/mol. The results obtained on H2 Qualitizer sampling 1 should be considered knowing that the cylinder valve was open before the HRS started its filling. The level of oxygen, nitrogen, and water (i.e., potential air ingress) may have been affected by the early opening of the cylinder valve.

As the sampling realised targeted different storage bank and due to the difference observed in the results, additional measurements were realised by MetroHyVe 2 partners on the actual hydrogen gas composition in the different storage banks.

The results were obtained few months after the sampling intercomparison. The storage bank compositions have evolved from October 2022 to June 2023. For example, the carbon dioxide, nitrogen, water or oxygen amount fractions showed completely different order of magnitude (e.g., nitrogen amount fraction is never over 254 µmol/mol in June 2023 while all sample in October 2022 were over 240 µmol/mol). Secondly, the storage bank received additional hydrogen (refilled) which makes difficult to assume what was the original composition of the hydrogen gas in October 2022. Therefore, the storage tank composition can't be directly used to determine the sampling representativity. The results showed trends observed in the sampling systems results.

Air Liquide sampling system sampled form the storage bank 3 which has the highest water and nitrogen amount fraction. Therefore, the result of their sampling is coherent with this observation.

The ENGIE sampling system has used storage bank 7 and 1 which had the second highest amount fraction of nitrogen and carbon dioxide respectively. It is coherent with their sampling results being the highest in nitrogen and carbon dioxide compared to the other systems, however the measured value tends to be higher than the expected amount fraction from the hydrogen amount fraction in the storage.

The HySAM sampling showed lower nitrogen and carbon dioxide amount fraction than Qualitizer sampling 2. It seems coherent as they used different fraction of storage bank 1, 2 and 6 (more storage bank 2 for HYSAM and more storage bank 1 for Qualitizer).

The Qualitizer sampling 1 used only storage bank 2 which had low water, nitrogen and carbon dioxide amount fraction and no oxygen. The results are coherent with a small ingress of air that may be due to the sampling start before the actual refuelling event started. The opening of the evacuated cylinder

may result into bringing unexpected gas from dead volume into the cylinder (different filling regime during the filling of the vessel from evacuated into system pressure).

Table 4. Measurement of nitrogen, carbon dioxide, water and oxygen from the five storage banks used in the intercomparison in October 2022. The sampling and analysis were realised in June/July 2023 by ZBT and NPL.

Storage bank	Measurement from storage bank realised in June 2023			
	Nitrogen amount fraction [ $\mu\text{mol/mol}$ ]	Water amount fraction [ $\mu\text{mol/mol}$ ]	Carbon dioxide amount fraction [ $\mu\text{mol/mol}$ ]	Oxygen amount fraction [ $\mu\text{mol/mol}$ ]
1	254	37	1.39	< 0.3
2	190	24	0.83	< 0.3
3	136	82	0.35	< 0.3
6	239	27	0.23	< 0.3
7	315	19.7	0.41	< 0.3

Table 5. Assumed storage bank composition based on June 2023 and dilution factor (considering dilution by high purity hydrogen).

Storage bank	Assumed storage bank composition based on June 2023 and dilution factor (considering dilution by high purity hydrogen)			
	Nitrogen amount fraction [ $\mu\text{mol/mol}$ ]	Water amount fraction [ $\mu\text{mol/mol}$ ]	Carbon dioxide amount fraction [ $\mu\text{mol/mol}$ ]	Oxygen amount fraction [ $\mu\text{mol/mol}$ ]
1	262	38	1.44	< 0.31
2	283	36	1.24	< 0.45
3	443	267	1.14	< 1.0
6	251	28	0.24	< 0.32
7	334	21	0.44	< 0.32

The water amount fraction is interesting as the amount fraction are significantly different from the actual storage amount fraction. Various reasons may account for these differences. First, at given temperature and pressure conditions at the HRS, hydrogen gas was in a pressure-dew point region where water may condense. This effect is dependent on the actual water amount fraction. Secondly, during the refueling process, the hydrogen temperature in the source storage bank and piping decrease due to rapid pressure change. These changes can lead to condensation of water in the hydrogen present in the storage tank. Third, the cooling unit required for FCEV refueling can influence the water amount fraction in hydrogen. The water amount fraction may decrease due to the actual temperature of the hydrogen gas passing in the cooling. Initial measurements already performed at ZBT show a significant decrease in water concentration by precooling the dispensed hydrogen. Therefore, the temperature of hydrogen gas sampled may be a parameter interesting to understand representativity.

Table 6. Evolution of water amount fraction in the hydrogen fuel of the different storage bank of ZBT HRS over time

Storage bank	water amount fraction [ $\mu\text{mol/mol}$ ] in December 2022	water amount fraction [ $\mu\text{mol/mol}$ ] in June 2023
1	29	37
2	18	24
3	49	82
4	13	-
5	15	-

6	36	27
7	27	19.7

Furthermore, the ambient temperature between the sampling intercomparison in October and additional analysis in June may also have an influence on the saturation of the water in the hydrogen (if liquid water is present). It may support an increase of measured water amount fraction in June compared to October.

Finally, the operation history of the HRS before sampling plays a possibly important role:

- Heat exchanger condition: the heat exchanger may influence the water amount fraction in the hydrogen gas due to the amount of water that may be already accumulated in it (e.g., duration of operation, heat transfer variation, separation and release of water, standby temperature is higher than T40 for example)
- Refueling frequency: in the case of consecutive sampling or refueling using precooling filling protocol, the dispensing line temperature would be much lower which may influence the temperature of the gas transferred and its water amount fraction.
- Condition of the storage banks: the temperature and pressure of the storage bank may differ due to a previous fueling or sampling. As explained it would impact the water amount fraction in the hydrogen.

In summary, the water amount fraction sampling at the HRS nozzle depends on many factors and can also change within a short time (e.g., change in ambient temperature, pressure, cooling used, mass flow rates, previous refueling etc.). As shown in the study, there is a lack of clarity in between water amount fraction in the storage and sampled by the different methodologies. It will be important to define the impact of these parameters to realize which one's impact significantly the sampling and need to be controlled or monitored.

A MetroHyVe partner (ENGIE) was able to perform online measurement of oxygen and water using Optical Feedback Cavity Enhanced Absorption Spectroscopy (Proceas, AP2E, FR) while the sampling was realised. The comparison of the measurement online with the offline results showed agreement for oxygen but the water amount fraction disagreed significantly. However, the online measurement did not agree either with the water amount fraction in the storage bank. The online water measurement corresponds to the average calculated during the last minutes of sampling to access the most stable measurement.. It would be interesting to realise further experiment to determine the origin of the difference (e.g., variation of water amount fraction during the sampling, analytical method difference).

Table 7. Comparison of ENGIE sampling results with the online measurement realised during these sampling events.

Component	ISO 14687:2019 Grade D (μmol/mol)	Measured amount fraction / (μmol/mol)			
		ENGIE Sampling 1	ENGIE measurement during sampling 1	ENGIE Sampling 2	ENGIE measurement during sampling 2
Cylinder reference	-	ECH-1	online	ECH-2	Online
Oxygen	5	0.69 ± 0.09	< 1.0	0.62 ± 0.08	< 1.0
Water	5	6.76 ± 0.34	3.4	4.45 ± 0.23	2.1
		6.58 ± 0.33		4.74 ± 0.24	

Establishing equivalence between online measurement and sampling followed by offline analysis requires additional study as these preliminary results already present some novel challenges.

Despite the complexity in realising a sampling intercomparison, the trends observed hints at possible equivalence between the sampling systems.

## Equivalence and representativeness of sampling system

Following the studies realised in MetroHyVe 2, it became critical to highlight the following recommendation for the different sampling system types:

### 1 Equivalence between serial and parallel sampling has progressed but some challenges remain.

- a. The comparison of serial sampling (ASTM D7606-17) and the parallel approach (H2 Qualitizer) showed equivalence for all compounds except water. However, the limit of detection of the laboratory performing the analysis was not sufficient to have a refined information on all compounds (i.e., nitrogen). Purging of parallel sampling system is a requirement to achieve equivalence.
- b. The comparison of serial sampling (Air Liquide sampling system) and parallel sampling (ENGIE sampling system, H2 Qualitizer and HySAM) showed equivalence for 9 out of 14 compounds. Differences observed on nitrogen, argon, carbon dioxide, oxygen and water may be related to the HRS (storage banks) and not to the sampling system. The storage bank trends were supporting this version. Further experiments are required to confirm the origin of the differences observed.
- c. The absence of reactive contaminants at the HRS used did not allow to check the ability of the system to sample reactive compounds (i.e., H<sub>2</sub>S, formic acid, ammonia). Despite the number of sampling realisation and the knowledge of hydrogen fuel quality in Europe and US, it has not been possible to create the condition for the testing. For such validation, it would either require access to a dedicated HRS that can achieve contaminated fuel. Such facility does not exist and would require significant research and development effort to develop a method to generate, certify hydrogen fuel quality and to ensure cleaning and decontamination afterwards. Another alternative would be to realise low-pressure small-scale validation in laboratory environment. Such alternative may be easier to implement in short term however the impact of the HRS pressure, filling rate or hardware will not be investigated and therefore would need further investigations.

### 2 Importance of understanding the impact of the HRSs parameters on the sample representativity: the study realised by MetroHyVe 2 consortium highlighted the impact of the HRS parameters on the sampling results and potentially on the representativity of the sample. It is critical for the sampling team to understand the following parameters of the station they work on:

- a. the station storage bank system: a serial sampling system may only sample a specific storage bank. It may not be representative of a refuelling event if the sampling team is not ensuring how the HRS filling protocol is designed (i.e., use of multiple storage bank). The parallel sampling approach is following SAE J2601 however it doesn't imply the sampling will achieve to sample all the storage bank. The storage bank sampled may vary based on their level and on the filling protocol, it is important to record information on the number of storage bank sampled and determine with the HRS station owner if it is representative of the process. The development of a sampling protocol may be advisable especially for complex HRS with multiple storage banks.

- b. the precooling temperature: the temperature variation between the different samplings were observed. Moreover, the precooling steps may have an impact on the actual water amount fraction. In the study, it was observed that water amount fraction was much lower for the sampling that showed low temperature. It is critical to record the actual precooling temperature of the sampling and ensure for serial sampling to achieve the same precooling temperature as for a FCEV fuelling event.
- c. the filling rate: the variation of filling rate was observed but it didn't seem to affect the results of analysis.
- d. Event prior to a sampling: consecutive sampling as sampling after a refuelling event may affect the temperature of the hydrogen gas sampled. It is important to take into consideration the events before the actual sampling in the reporting as it may influence the results.

### 3 Transport and cylinder handling

- a. Transfer of samples into smaller canister is often used to transport small quantities of hydrogen. Therefore, any loss during sample transfer is critical. In the study realised in US, DMS transferred the H<sub>2</sub> Qualitizer sample into a smaller canister, the results obtained were equivalent to the original sample. The drawback was the absence of reactive compounds which does not support evidence that reactive compounds can be transferred without losses. The MetroHyVe 2 study in Annex A showed that there was significant difference between decanted and decant cylinder for several reactive compounds (H<sub>2</sub>S, formic acid, formaldehyde, and water). Several aspects of the transfer methodology are highlighted by the study:
  - i. transfer procedure: evacuating and venting procedure with cylinder purges not being the ideal method for purging the line. Due to the very low levels of contaminants present in the system any small loss of contaminant can be significant.
  - ii. type of connection: it is critical aspect as air ingress may happen due to improper purging (e.g., difficulty to purge quick connect using cycling purge methodology). It is, therefore, recommended to use a flush through method when using quick connect connectors to ensure they are properly purged or to prefill cylinder with high purity hydrogen. Otherwise, normal connection did not show similar issues, but it requires leak checking.
  - iii. the sampling cylinder type: the cylinder passivation is important (for example, formaldehyde measured amount fraction was significantly different between the Sulfinert<sup>®</sup> cylinder and the Silonite<sup>™</sup> cylinders). Selection of the decant cylinders based on their performance is required to keep trace amount fraction. However, it is not always possible to find suitable cylinder (e.g., formic acid in hydrogen). In this case, decant cylinder is not recommended due to the loss of the compound of interest and biased results.

The transferred of samples was considered suitable for inert gas (including nitrogen) however it requires dedicated and validated procedure for the reactive compounds (e.g., formaldehyde, formic acid, water, H<sub>2</sub>S).

- b. Cylinder transport: it has been a bottle neck for the comparison in the US. It was mainly related to the packing and labelling of the dangerous goods (compressed



hydrogen). For transport application, the cylinders or canisters should be compliant with the local and international transport regulations. Moreover, it is mandatory that the documentation for transporting the cylinders is realised by authorised and trained staff. Without such documentation, the hydrogen samples were blocked for months in US before their returns to Europe. The documentation includes the dangerous goods note, packing and labelling of the goods, dispatch notes, packing list, SDS. Transport of compressed hydrogen into vehicles is regulated and requires to be in compliance with the local regulations and the Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR).

## Cylinder preparation, decontamination and carry over

The MetroHyVe 2 partners studied the potential carry over between sampling cylinders. During the hydrogen fuel sampling, the laboratory may not always use a new cylinder. Therefore, it is important to ensure that the preparation of the cylinder remove any traces of the previous sample especially if it was contaminated by sulphur or water. Three preparative methods were investigated to determine if they could remove high content of H<sub>2</sub>S and water from contaminated cylinder (synthetic contamination). The three methodologies were able to remove all traces of sulphur and water to a level below the detection limit of the partner analyser. Therefore, the three methodologies are suitable for preparing sampling cylinder for hydrogen fuel quality sampling. Any alternative preparative method may require equivalent evidence to ensure that there is no carry over between samples.

## Good practices summary

### Cylinder preparation

Two types of cylinder preparations have been used: prefilled cylinder with ultra-high purity hydrogen or evacuated cylinder.

Prefilled cylinders with ultra-high hydrogen purity require proper venting of the high purity gas in the cylinder prior to sampling. If some of the prefilled gas is remaining in the cylinder, the impact of such volume should be taken into consideration in the calculation of the final amount fraction in the sample.

The evacuated cylinder shall only be open once the HRS starts providing hydrogen. If evacuated cylinder is open before the HRS is fully delivering (not pressure pulse), it may result in biased results through air ingress, insufficient purging, flow dynamic due to the vacuum.

Cleaning of cylinder between samplings, three methodologies tested by MetroHyVe 2 partners (Report 3.1.7) are suitable for preparing sampling cylinder for hydrogen fuel quality sampling. Any alternative preparative method may require equivalent evidence to ensure that there is no carry over between samples.

### Choice of sampling system

The two strategies, parallel and serial sampling, have advantages and disadvantages. The important aspects to consider are:

- Type of events
  - o Routine verification: parallel and serial sampling strategy are suitable. The sampling duration is faster for parallel sampling strategy as it doesn't require the HRS to be set in maintenance mode. Parallel sampling may be considered as less disturbing to the actual normal operation of the HRS.

- Poor quality incidents or unknown/new site untested within the industry: the parallel sampling systems requires to use a FCEV or mock-up tank as a sink. In case of known issues at HRS, it is critical to ensure that the FCEV used is not exposed knowingly to contaminants as it may impact FCEV performance and lifetime. The use of parallel system may not be recommended to investigate poor quality incidents except if a mock-up tank is used. Serial sampling systems are more suitable option as no FCEV is required for such investigations.
- Complexity of the HRS (i.e., number of storage bank)
  - Simple HRS with one storage bank: the parallel and serial sampling will allow representative sampling of the system.
  - Multiple storage bank HRS: the parallel sampling system achieve to follow a FCEV refuelling and therefore is prompt to sample a more representative fuel from the HRS however it should be verified as in some case it may only represent a small part of the system (one storage bank out of seven). Serial sampling sample one storage bank. It may be possible to sample multiple storage bank as the HRS is set in manual mode. It has to be implemented by the HRS operator.
- Access to HRS maintenance mode (through HRS operators and override)
  - Accessible: serial sampling and parallel sampling strategy can be used. It requires the presence of an HRS owner operator or remote control.
  - Not accessible: parallel sampling strategy can be used in HRS in normal operation. Serial sampling has been realised using the pressure pulse of the HRS. The HRS realising that there was no FCEV or mock up tank and therefore not realising any refuelling. It has been realised but it is not recommended due to safety concerns for the sampling equipment and the operators.

### Realisation of sampling

- Purging: parallel and serial sampling strategy require proper purging and venting in safe condition. The use of portable vent for the purging and in case of the activation of the pressure relief valve is required. Alternatively, connection to the HRS vent should be used.
- Definition of the HRS condition for sampling
  - Parallel sampling: the FCEV dimension and the tank level should be recorded to ensure sufficient gas is sampled. The filling protocol (temperature, filling rate, mass) and the storage bank sampled should be obtained from the HRS owner to validate the representativity of the sampling.
  - Serial sampling: the parameters of the HRS during the sampling should be defined in advance and include, the pressure delivered by the HRS, the temperature of the precooling, the storage bank to be sampled.

### Sample handling and transport

- Transfer of cylinder for additional investigation by offsite laboratory. The transfer of an original cylinder into another canister type may be realised. The study demonstrated that most inert compounds were unaffected, however reactive compounds (e.g., H<sub>2</sub>S, water, formic or formaldehyde) requires validated methodology and cylinders to avoid sample changes (loss or increase). Further investigation would be required for developing robust methodology for transfer of all reactive species without changes.
- Sampling staff should be trained to handle and prepare all documentations for the transport of dangerous goods according to the international and local regulations. A safe storage should be

available in case the transport company is not able to pick up the gas samples just after the completion of the sampling.

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## Annex A – MetroHyVe 2 decant study

The Metrohyve 2 partners realised a cylinder decant study in laboratory to gather new evidence on decant procedure and impact on reactive species at low amount fraction (nmol/mol level) in hydrogen gas.

### Experiment set up

The study was designed to investigate potential losses of contaminant from sample cylinders if the original sample is decanted into a smaller vessel for analysis. To investigate the different possibilities of decanting set ups three conditions were agreed to be tested.

The three setups selected were as follows:

- i. Decant method 1 –Using a pressure regulator with a stem connector attached to the ‘parent’ cylinder and non-treated stainless-steel tubing to connect to the ‘daughter’ cylinder. It uses standard non treated parts and pressure regulator with large dead volume, it simulates a standard procedure.
- ii. Decant method 2 - Using a stem connector from the ‘parent’ cylinder being decanted and non-passivated stainless-steel tubing to connect to the ‘daughter’ cylinder with no pressure regulation. It uses standard treated parts and regulator with large dead volume, it simulates a better procedure for reactive gas.
- iii. Decant method 3 - Using an NPL minimum dead volume connector (MDV) and a passivated stainless-steel tubing to connect the ‘parent’ cylinder to the ‘daughter’ cylinder with no pressure regulation. It uses special treated parts and has the lowest dead volume (no pressure regulator), it simulates an optimised procedure for reactive gas.

### Materials and methods

#### Cylinder materials

The sampling vessels selected for the ‘daughter’ cylinders for the decant were 1L stainless steel Sulfinert® (Resteck, US) treated cylinders fitted with Sulfinert® treated valves (Swagelok, UK) and 0.3L Silonite™ treated stainless steel cylinders (Entech, NO). The ENTECH cylinders has quick connect connection (Swagelok, NO) on both ends.

#### Decanted cylinder composition

The cylinders were filled by decant of high pressure cylinder to a target pressure of 60 bar. The cylinder selected to be decanted was the cylinder D028953R. It was prepared as part of the MetroHyVe 2 activity A3.1.5. The cylinder contained the target composition as shown in Table 1 below.

Table 1: Target composition of the decanted cylinders

Contaminants	Threshold value / $\mu\text{mol mol}^{-1}$ (EN 17124:2018)	Cylinder amount fraction / $\mu\text{mol mol}^{-1}$
N <sub>2</sub> (Tracer)	300	900
HCl	0.05	0.1
H <sub>2</sub> S	0.004	0.008
HCHO	0.2	0.4
HCOOH	0.2	0.4
H <sub>2</sub> O	5	5

<https://www.sintef.no/projectweb/metrohyve-2/>

### Cylinders decant equipment

The pressure regulator (BOC, UK) used for the decant method 1 had an output pressure of up to 250 bar to allow the 60 bar fill pressure required to be transferred. All materials used in Decant method 1 and 2 were stainless steel (Swagelok, UK).

In Decant method 3, the treated material was Sulfinert<sup>®</sup> treated (Swagelok, UK). The minimum dead volume connector is made by NPL and treated Silconert2000 (Restek, UK).

Figure 1 shows a schematic of the setup of the experiment and Figures 2-4 show pictures of the set up for each condition selected for the study. The Sulfinert<sup>®</sup> cylinders will be referred to as Cylinder A and the Silonite<sup>™</sup> cylinders will be referred to as Cylinder B.

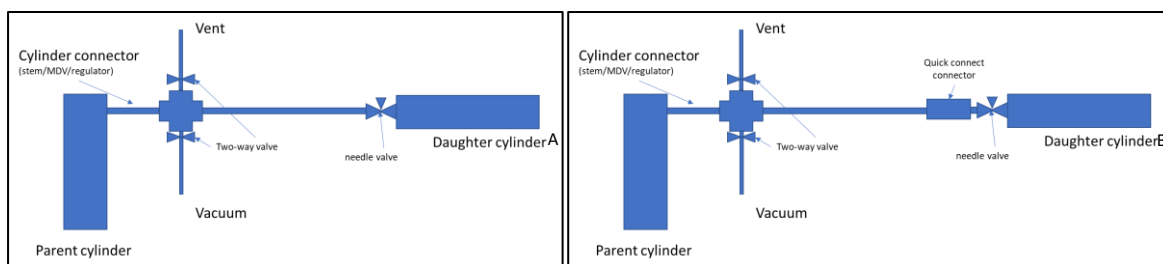


Figure 1. Diagram on the set up of the decant study with the Sulfinert cylinder (cylinder A) and with the Silonite<sup>™</sup> cylinder (cylinder B).

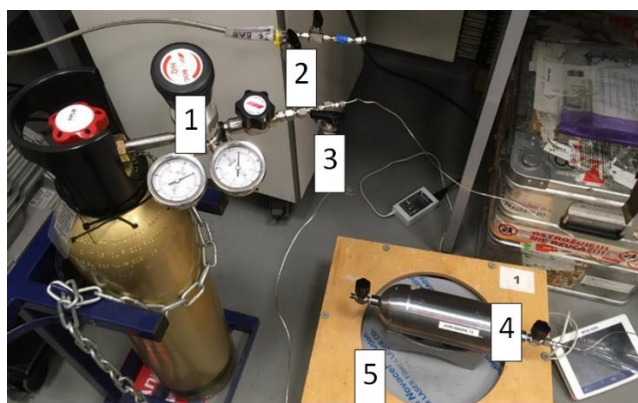


Figure 2. Picture of the decant set up with regulator and untreated tubing conditions. 1 represents the pressure regulator, 2 is the connection to the vacuum, 3 is the connection to the vent, 4 is the decant cylinder (Sulfinert cylinder A), 5 is the weighing balance.

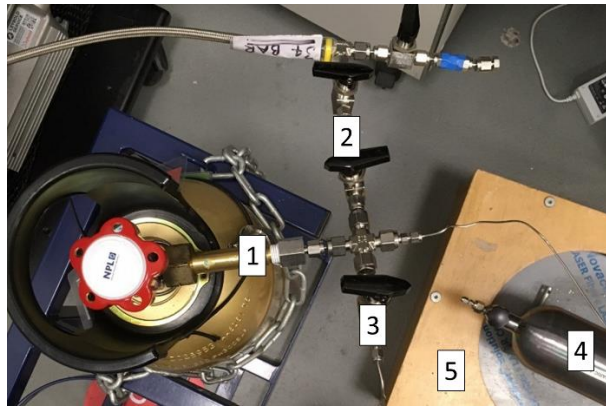


Figure 3. Picture of the decant set up for using an untreated stem and tubing. 1 represents the stem connector, 2 is the connection to the vacuum, 3 is the connection to the vent, 4 is the decant cylinder (Sulfinert cylinder A), 5 is the weighing balance.

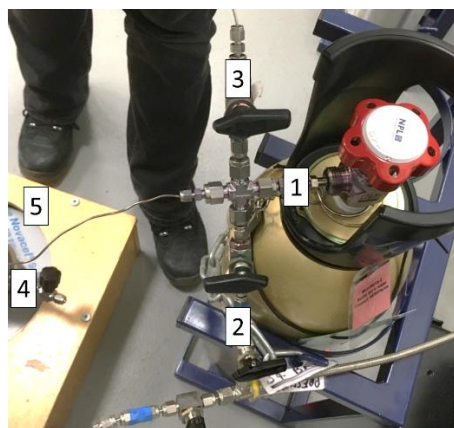


Figure 4. Picture of the decant set up for using treated connections and tubing. 1 represents the stem connector, 2 is the connection to the vacuum, 3 is the connection to the vent, 4 is the decant cylinder (Sulfinert cylinder A), 5 is the weighing balance.

#### Cylinder decant procedure

To reduce the number of wetted surfaces during the decant transfer the transfer of gas to 60 bar was done by gravimetry. This meant an additional connection with a pressure gauge was not required. Before the decant experiment, the cylinders were evacuated for at least 12 hours to a vacuum of below  $5 \times 10^{-7}$  mBar. The purging of the line was conducted using the following steps. The line is evacuated before pressurising to at least  $8.5 \times 10^{-6}$  mBar. Then, the line is pressurised with sample gas from the 'parent' cylinder. The pressure in the line is released through the vent line. The line is evacuated again  $8.5 \times 10^{-6}$  mBar. The previous steps are repeated, for a total of two cycling purges with the sample gas and a total of three evacuations of the filling line. Then, the mass transfer was monitored using a XPR32001L balance (Mettler Toledo, UK). A mass of 4.75 grams for transfer into the 1L Sulfinert® vessels and target of 2.2 grams into the Entech vessels was targeted. Two cylinders for each condition were filled, one of the Sulfinert® type and one of the Entech type, leading to a total of six cylinders filled during the decant study.

#### Analytical methods

The water amount fraction was measured on a quartz crystal microbalance, QMA401 (Michell, US). Gases are sampled directly from the gas cylinder to the analyser, via a HF series pressure regulator (3.4 bar outlet) (Swagelok, UK) and a second high precision flow regulator (model: RP10SS-MSB-0240-

SW1/4"-040, LNI Schmidlin, CH) that was used to keep the pressure at 1 bar gauge into the analyser (flow to 0.333 L/min).

The hydrogen sulphide amount fractions were measured on a GC-SCD (Agilent, UK). The method used a HP-1 column (60 m x 0.530 mm) with helium carrier. The sample loop size used for injection was 5 ml. The hydrogen sulphide amount fractions were quantified using a calibration curve produced using a dynamic reference of hydrogen sulphide. The dynamic references were produced through the dilution of a NPL PRM (1  $\mu\text{mol/mol}$  hydrogen sulphide in hydrogen) into high purity hydrogen (purity 99.9999%, BIP+, Air Products, US) using a mass flow controller system (Bronkhorst, NL).

The formaldehyde amount fraction was analysed using SIFT-MS, Voice 200 Ultra (Anatune, UK). The reagent ion used was  $\text{H}_3\text{O}^+$  and the reaction product measured was  $\text{CH}_3\text{O}^+$ . The formaldehyde amount fraction was quantified using a dynamic reference. The dynamic reference was produced through the dilution of a NPL PRM (11  $\mu\text{mol/mol}$  formaldehyde in hydrogen) into high purity hydrogen (purity 99.9999%, BIP+, Air Products, US) using a mass flow controller system (Bronkhorst, NL).

The formic acid amount fraction was analysed using SIFT-MS, Voice 200 Ultra (Anatune, UK). The reagent ion used was  $\text{H}_3\text{O}^+$  and the reaction product measured was  $\text{HCOOH}_2^+$ . The formic acid amount fraction was quantified using a dynamic reference. The dynamic reference was produced through the dilution of a NPL PRM (40  $\mu\text{mol/mol}$  formic acid in hydrogen) into high purity hydrogen (purity 99.9999%, BIP+, Air Products, US) using a mass flow controller system (Bronkhorst, NL).

Oxygen and argon for the air investigation were measured using a 7890A gas chromatograph (GC) (Agilent Technologies, UK) coupled with a pulsed discharge helium ionisation detector (VICI, CH). The method used two Molesieve 5A capillary columns, one 30 m x 0.53 mm x 0.50  $\mu\text{m}$  and one 50m x 0.53 mm x 0.50  $\mu\text{m}$  with helium carrier gas. The loop size used for sample injection was 1 ml.

### Results of the decant study

The decanted cylinders were analysed for the selected compounds in the following order, hydrogen sulphide, water, formic acid, and formaldehyde. The other compounds present in the decanted cylinder were not analysed due to low volume of gas.

#### Impact of cylinder decant on Hydrogen sulphide amount fraction in hydrogen

Hydrogen sulphide was analysed first due to the high impact on fuel cell performance and the reactivity of the compound.



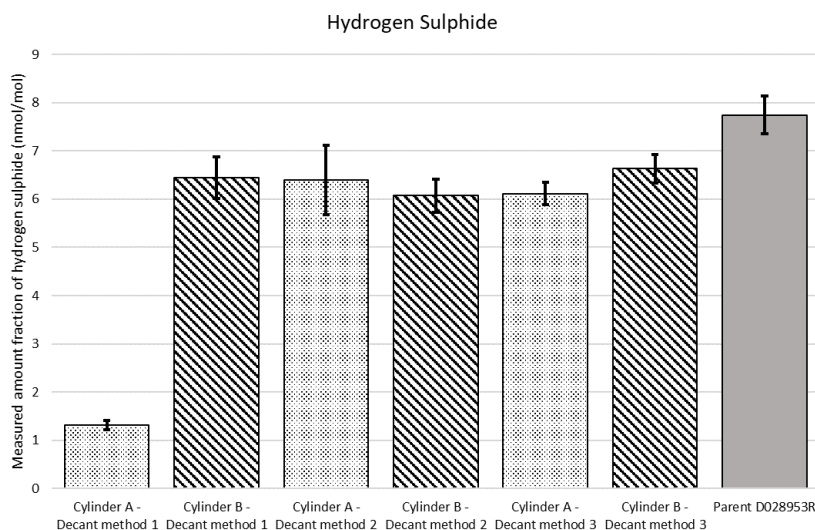


Figure 5. Graphic showing the measured amount fraction of hydrogen sulphide compared to the decanted cylinder D028953R (solid grey bar). Bars with dotted pattern represent cylinders A and bars with striped pattern are cylinders B.

All decant cylinders showed a measurable loss of hydrogen sulphide amount fraction from the amount fraction measured in the parent cylinder. The cylinder A from Decant method 1 had a significantly larger amount fraction loss than all other decant cylinders. This cylinder was the first decant through the untreated line, it may be possible that adsorption of H<sub>2</sub>S occurred on the surface of the transfer line. The absence of such effect on the next decant may be related to saturation of the adsorption site during the first decant (e.g., enough H<sub>2</sub>S has saturated all the adsorption sites of the transfer line 1). Therefore, the next decant benefited from this first decant experiment. It highlights that the methodology used for Decant method 1 did not realise sufficient exposure of the transfer line (e.g., cycling purges) to avoid adsorption. As the second decant experiment showed better results, at least doubling the number of cycling purges is required for decant method 1.

In comparison, treated system as Decant method 2 and 3 didn't have a large loss as seen for the non-treated system. Decant method 2 and 3 reached more than 75% transfer yield of H<sub>2</sub>S. It demonstrates the importance of the surface passivation for H<sub>2</sub>S transfer.

However, H<sub>2</sub>S amount fraction in the decanted cylinders from Decant method 2 or 3 agreed with the decanted cylinder (D028953R). Further studies are required to improve the decant method for transfer of H<sub>2</sub>S to achieve 100% recovery yield.

#### Impact of cylinder decant on water amount fraction in hydrogen

The water amount fraction was measured in all decant cylinders as shown in Figure 6. Water is a prominent contaminant due its high likelihood of occurrence in real samples. As shown in the figure below, decant samples showed a measurable increase in water compared to the water amount fraction of water in the parent cylinder D08953R.

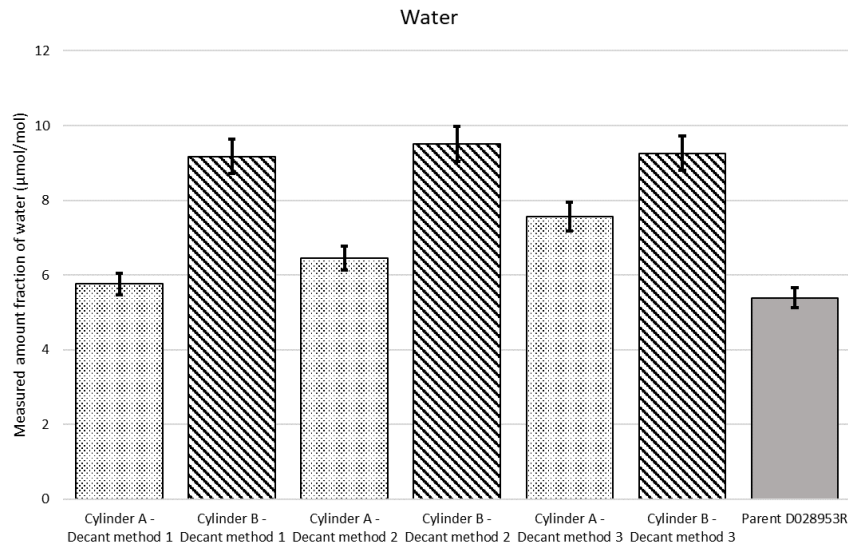


Figure 6. Graphic presenting the measured amount fraction of water in the decant samples compared to the parent cylinder D028953R (solid grey bar). Bars with dotted pattern represent cylinders A and bars with striped pattern are cylinders B.

An increase of water amount fraction may be related to airborne contamination during the decant experiment (e.g., insufficient purging). To investigate it, three of the samples were analysed for oxygen and nitrogen (see Figure 7). The cylinders chosen were “Decant method 1 cylinder A” (only cylinder without any significant increase of water amount fraction), “Decant method 3 - cylinder A” (measurable increase of water amount fraction) and “Decant method 3 - cylinder B” (measurable increase of water amount fraction).

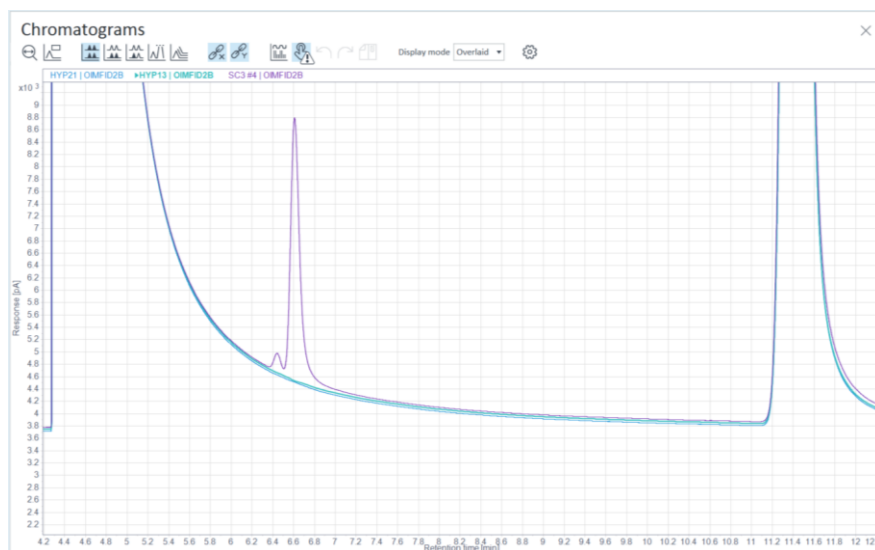


Figure 7. Chromatograms of the decant cylinders being analysed for air. The peak at 4.4 minutes is the matrix hydrogen, the peak at 6.6 minutes show argon, the peak at 6.7 minutes shows oxygen and the peak at 11.7 minutes shows nitrogen (present in the samples as tracer). The Blue chromatogram is “Decant method 3 - cylinder A”, the green chromatogram is Decant method 1 cylinder A and the purple chromatogram is Decant method 3 - cylinder B.

The argon and oxygen peaks present in the “Decant method 3 - cylinder B” sample show the presence of air in the cylinder. As air also contains water a small ingress of air into the cylinder could explain the large increase in measured water. The air ingress may be due to the presence of quick connect connectors to the cylinder B as the purging procedure was done as cycling with evacuation so may not have fully purged the air. This shows that if using cylinders with quick connect for decanting it may be

Good practice guide for hydrogen quality sampling procedures/methods at HRS nozzles (harmonised with USA and Japan)

better to flush through the connections and the cylinder to ensure the quick connect connectors are purged sufficiently.

The cylinder “Decant method 3 - cylinder A”, however, shows no air but showed increase in measured water amount fraction. It is possible that the evacuation of the line was sufficient to remove the oxygen and nitrogen but not the water.

#### Impact of cylinder decant on formaldehyde amount fraction in hydrogen

Formaldehyde is a reactive contaminant with known stability problems. The results presented in Figure showed that the formaldehyde amount fraction in cylinder A was equivalent to the decanted cylinder with all the decant methodologies. However, a loss was observed with cylinder B using similar decant methodologies. It hinted to a difference in measured amount fraction between the Cylinder A and B. This may be due to stability of the formaldehyde in the cylinders rather than loss during transfer. Due to the other measurements prioritised (sulphur and water), the decant cylinders were analysed for formaldehyde two weeks after the decant was conducted.

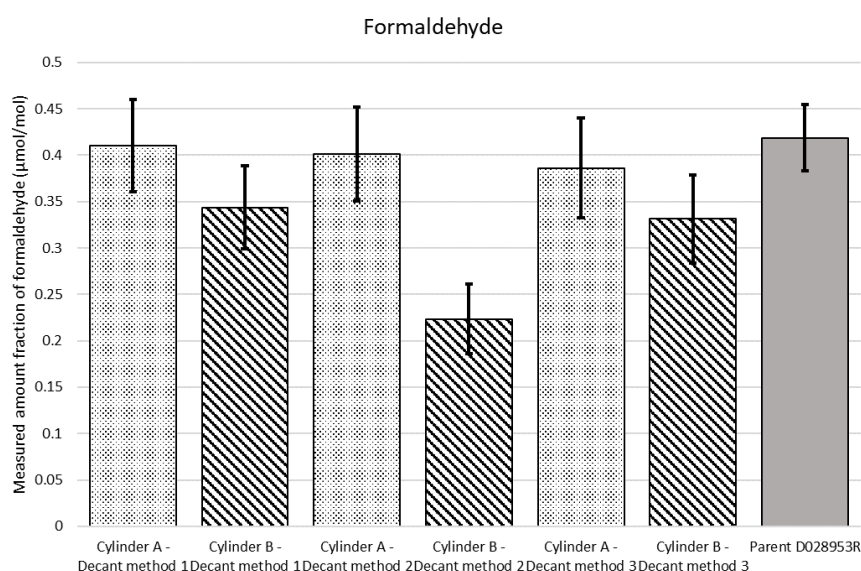


Figure 8. Bar chart showing the measured amount fraction of formaldehyde in the decant samples compared to the parent cylinder D028953R (solid grey bar). Bars with dotted pattern represent cylinders A and bars with striped pattern are cylinders B.

These results highlighted the important of selecting the cylinder in which the stability of the contaminant being measured is known.

#### Impact of cylinder decant on formic acid amount fraction in hydrogen

Formic acid is a reactive contaminant with known stability problems. Figure 9 shows a loss of formic acid amount fraction in decant cylinders A and B compared to the decanted cylinder (D028953R). The cylinders B seem to have a larger loss of formic acid than the cylinders A. It may relate to the actual cylinder passivation being less suited to stabilising formic acid in hydrogen rather than the actual decant methodologies.

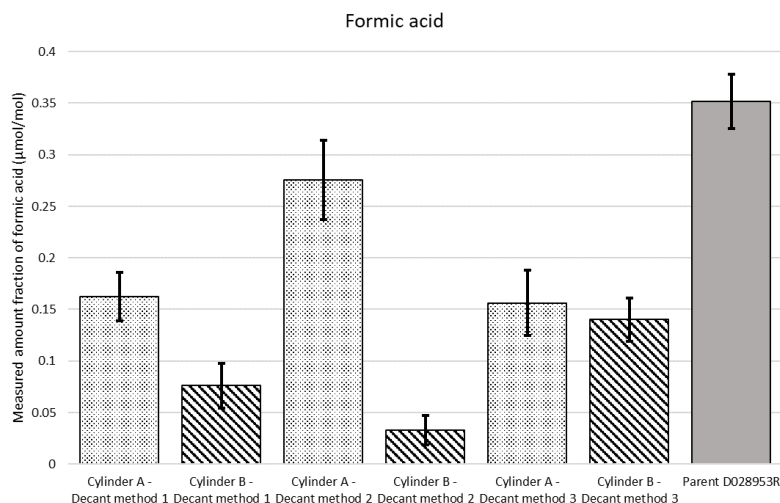


Figure 9. Bar chart showing the measured amount fraction of formic acid in the decant samples compared to the parent cylinder D028953R (solid grey bar). Bars with dotted pattern represent cylinders A and bars with striped pattern are cylinders B.

These results highlighted the importance not to decant or transfer hydrogen sample for the analysis of formic acid in hydrogen.

### Conclusion

The results from the decant study highlighted the challenges associated to cylinder decanting. The results from the study showed that for 3 out of 4 reactive compounds the decant cylinder was not equivalent to the original sample. The study highlighted that the decant methods presented were mostly equivalent (except for the decant method 1 that requires additional purging for H<sub>2</sub>S). The study highlighted the requirement to ensure sufficient purging or adjusted protocol (i.e., flow through purging when using quick connect). The cylinders could also be prepared with a small volume of pure hydrogen within them to stop the vacuum inside the cylinder drawing air into the sampling vessel.

The study also highlighted the impact of the cylinder passivation (difference between Sulfinert® and the Silonite™ cylinders). In this study, formaldehyde was better decanted in Sulfinert® cylinder than in the Silonite™ cylinders.

Several parameters influence the decant results: choice of cylinder (e.g., loss without the appropriate passivation), type of connection (e.g., difficulty to purge quick connect using pressure cycles), the methodology (e.g., insufficient number of purges may lead to increase of air or water). The results may be a loss (e.g., formic acid) or a gain (e.g., water) in measured amount fraction compared to the original samples. Such outcome will lead to biased results to the end user.

The development of appropriate methodology for decanting / transferring hydrogen sample into smaller canister is required based on the results of this study and the importance of hydrogen fuel sample analysis.