METROLOGY for HYDROGEN VEHICLES

REPORT:

Good practice guide for sampling at an HRS including a potential method for the determination of losses of particles in hydrogen gas passed through a regulator system

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www.metrohyve.eu

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1 Introduction

1.1 Task objectives under MetroHyVe

The aim of this task is to identify the available technology for particle sampling at a hydrogen refueling station (HRS) and to develop a method for testing the particle losses caused by the introduction of a regulator system to a sampling setup. A new method will be devised to generate a particle laden stream of hydrogen gas and a system will be designed to deliver the gas and particles to the PALAS® OPC system [1]. Tests will be performed to assess the suitability of these methods, and the results will be used to write a good practice guide for this procedure with focus on traceability, accuracy and good practice.

1.2 Scope of the Good Practice Guide

Particulate contamination is found in hydrogen, introduced through the production of the hydrogen gas or from the degradation of transportation and storage equipment [2], [3], [4], [5]. These particles can be destructive to fuel cells so efforts must be made to monitor, fully characterize and ultimately eliminate them. A traceable, reliable and repeatable method for the determination of the mass concentration of the particulates in a volume of gas is required. Filters have long been used to collect and measure particulate matter in the area of ambient air monitoring and can, therefore, be considered as a reliable method to measure the particulate matter in a gaseous medium. This Good Practice Guide is intended to be used as helpful document for those wishing to set up their own measurement system for the determination of particulates in hydrogen. This guide will also highlight the considerations, quality control and procedures required for accurately assessing the effects of the introduction of regulators into testing systems.

1.3 Particulate contamination causes and issues

The concentrations of impurities in fuel grade hydrogen gas must be tightly controlled and carefully monitored to ensure the optimum operation of vehicles which utilize hydrogen as a fuel. The limits for various impurities have been set by the International Organisation for Standardization (ISO), with a limit of 1 mg Kg^{-3} set for particles [6]. To date, there are no online, real-time measurement techniques for the measurement of the particulate content of a hydrogen gas stream. The standard method is to collect particles on a pre-weighed filter and determine the mass of particles in the gas stream by reweighing after sampling [7].

Particles in the hydrogen gas can originate from a number of different sources, potentially related to the initial fuel source, production methods and storage methods [3], [4], [5], [6]. Contamination of the initial fuel source used during the production of hydrogen gas with compounds such as water, ammonia, sulfur compounds or formic acid [3] can lead to the formation of acids or salts within the gas stream or on the surfaces of storage units or fuel cell components [4], [5], [6]. These impurities must be removed in order to reduce the possibility of degradation of the fuel cell and the corrosion of storage containers which could potentially introduce metallic particles into the gas stream [4]. The production process could also introduce particles into the fuel gas. For example, the pyrolysis and gasification of biomass to produce hydrogen gas can lead to tar formation, this could potentially lead to carbonaceous particles occurring in the gas stream [6].

In order to minimize the concentrations of particles in the hydrogen gas stream, rigorous decontamination of the initial fuel source and subsequent products of the various methods must be carried out. The selection of appropriate storage and transportation methods could also potentially minimize any particle contamination of hydrogen fuel which can potentially have serious operational, financial and health repercussions. Decreased performance of the fuel cell or the degradation of the fuel cell components could lead to significant environmental and public health issues in terms of emissions from the vehicle. Rectifying these issues in the fuel cell represents a significant financial benefit as a result of reduced fuel contamination.

2 Sampling Procedure

2.1 HYDAC PSA-H70

The use of the HYDAC PSA-H70 was examined in detail in the previous MetroHyVe report 'A4.2.1: A review of existing particulate sampling techniques at hydrogen refuelling stations' [8]. The second generation of this sampling apparatus has been successfully tested at an HRS and the operation guide is available on the MetroHyVe website at www.metrohyve.eu. The Particle Sampling Adapter-H70 is a device that can be attached to the hydrogen refuelling station at the nozzle in order to collect particulate contaminants onto a filter at the point of refuelling at a pressure of 700 bar, for subsequent off-site mass analysis. What makes this device unique is that the PSA-H70 is designed to be used at high pressures so the hydrogen does not first need to pass through a pressure regulator which would potentially incur particulate losses.

The PSA-H70 conforms to ASTM D7650; the "Standard Test Method for Sampling of Particulate Matter in High Pressure Hydrogen used as a Gaseous Fuel with an In-Stream Filter" and is able to sample for ensuing particle analysis according to ASTM D7651; the "Standard Test Method for Gravimetric Measurement of Particulate Concentration of Hydrogen Fuel".

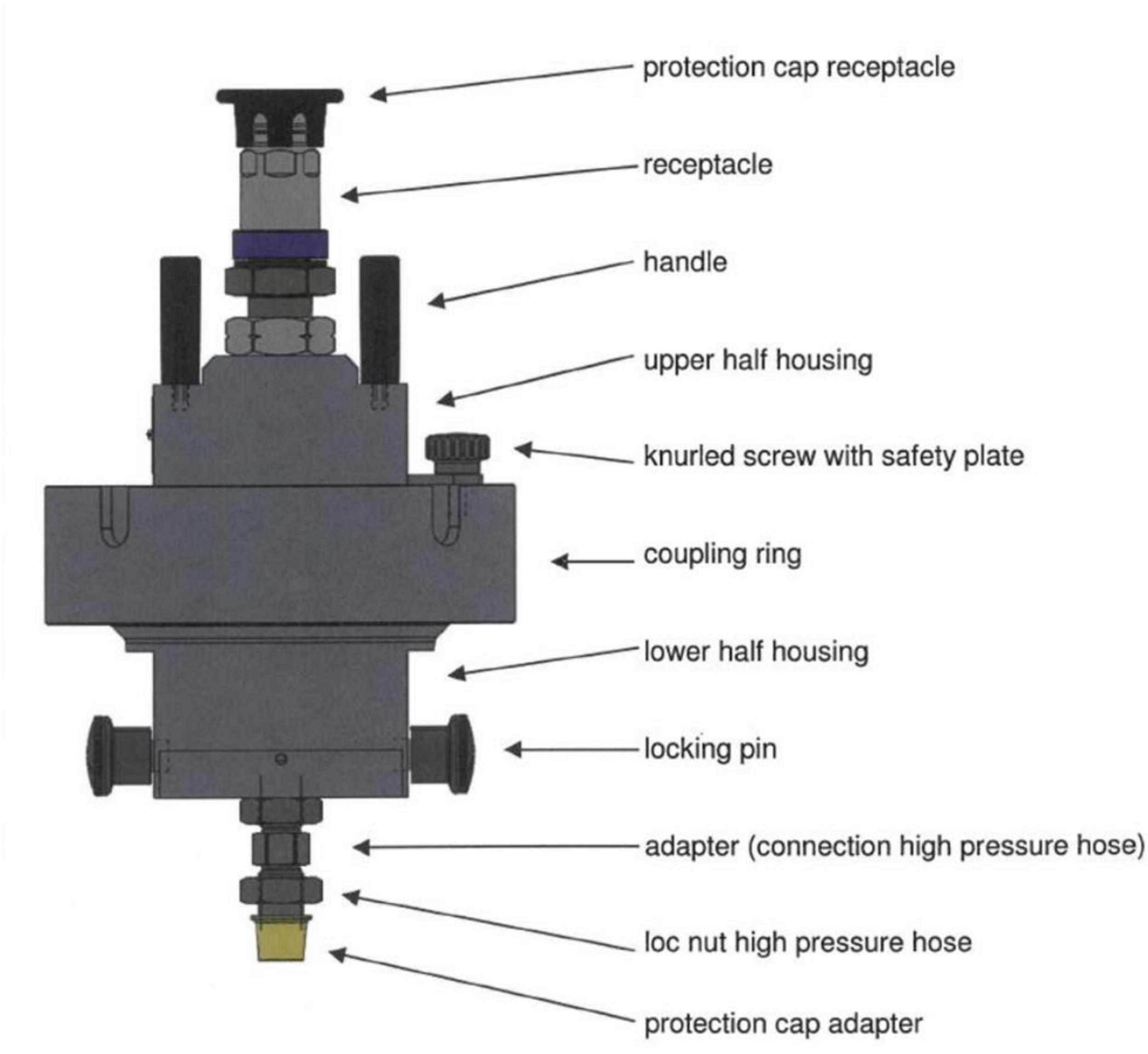

Figure 1: Schematic of second-generation PSA-H70

The PSA-H70 is connected to the hydrogen filling station. To ensure there are no leaks, a test pressure pulse of (approx.) 800 bar is applied. A manually operated throttle protects the sintered filter support from overloading during the pressure test. The filter membrane, a hydrogen-compatible PTFE filter, catches particulates within the hydrogen stream. The filter can then be removed and weighed in a controlled laboratory environment. Mass gain above the calculated error of the weighing procedure can then be attributed to particulate contaminants found on the filter membrane from the hydrogen stream during the filling procedure. The system can also be used for 350 bar systems.

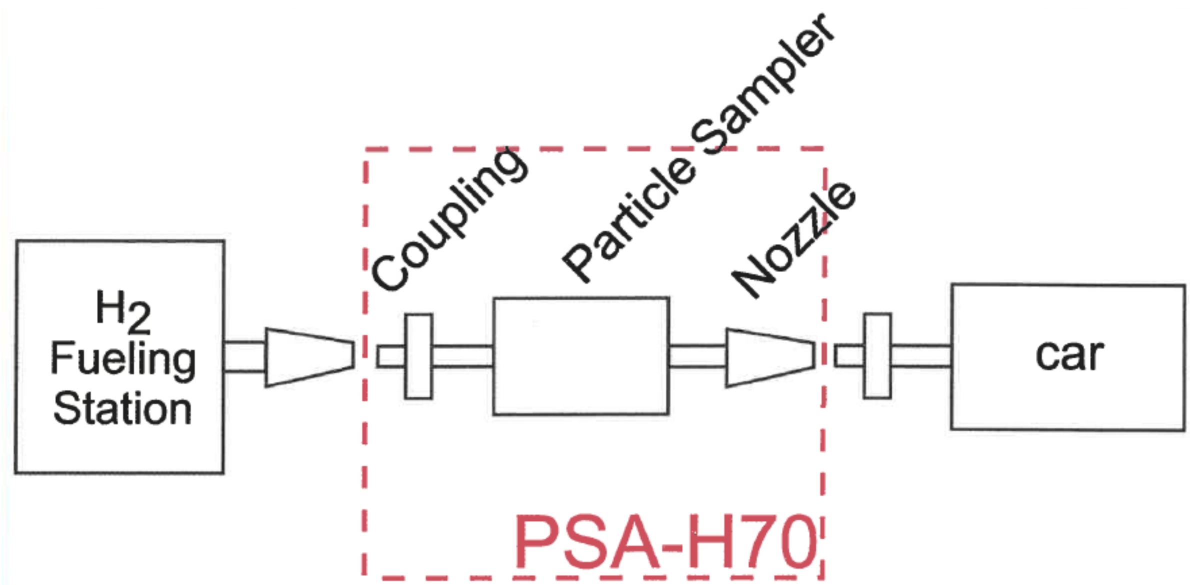

Figure 2: Positioning of the PSA-H70 in the HRS

2.2 Setup of testing for measurement of particle laden hydrogen gas from a cylinder

In addition to understanding the potential sources of particles in a sample of gas, it is important to consider the potential impact of the sampling system being used. The sampling system being used may result in particle losses before the sample reaches the detector. In order to assess the potential losses, the system shown below was designed. A comprehensive risk assessment was conducted prior to the design and construction of the testing system. The considerations below highlight some of the mitigation actions introduced in an effort to reduce the risks associated with utilizing the Optical Particle Counter (OPC) and hydrogen gas.

- The OPC generally operates with a flow rate of 5 l min^{-1} drawn from an external vacuum pump. In order to reduce the amount of hydrogen gas used, and to mitigate the risks associated with using a pump with hydrogen, the pump was removed from the system and the flow of gas through the system was controlled using a hydrogen rotameter.
- A 3m tall exhaust line was attached to the outlet of the pump, featuring a flame damper and diffuser at the outlet. This will prevent the potential build-up of hydrogen gas at the outlet and prevent any ignition of the hydrogen gas in the sampling system.
- The system was designed using exclusively stainless-steel tubing and stainless-steel Swagelok® fixtures, with the exception of the exhaust line.
- In the HPA, a suspension of deionised water and polystyrene latex (PSL) beads, with a nominal size of 0.9 µm (0.903 µm ± 0.012 µm), was deposited. These PSL beads are NIST traceable and are characterized under electron microscopy to determine their size distribution.

2.2 Equipment

The equipment used in this experiment were as follows:

2.2.1 Optical Particle Counter (OPC)

The OPC used during this experiment was the PALAS® Promo 2000 P model [1]. This model has a separate sampling head, which can be located away from the main instrument which contains all of the electronic components. This makes them ideal for measurements at sites where a flammable atmosphere could cause an issue. In these models, as only light is transmitted between the measurement head and the instrument body, this makes the head intrinsically safe and perfect for use with a flammable gas such as hydrogen. The sampling head used for this testing was graded for high pressure sampling, denoted by the “P” in the model name.

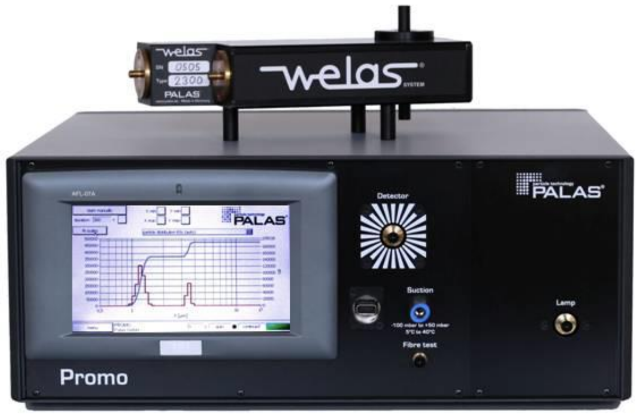

Figure 1: PALAS® OPC model 2000 P system

2.2.2 High Pressure Atomiser (HPA)

A TOPAS® high pressure atomiser (HPA) model ATM 210 was used as the method of particle generation during this experiment. One major advantage of using an atomizer such as this is that it does not require electricity and so is intrinsically safe for flammable gases such as hydrogen. One issue is to generate a stable particle concentration of a known size distribution in gaseous hydrogen. The primary difficulty with this is that it must be generated in situ as particles added to a pre prepared cylinder of hydrogen would be lost to the walls of the cylinder. Additionally, generating particles above 300 nm to add directly to a gaseous hydrogen stream is non-trivial.

Figure 2: TOPAS atomizer ATM 210 system

2.2.3 Two-Stage Hydrogen Regulator

A two-stage stainless steel hydrogen regulator from CONCOA was used in this experiment. The regulator was kept fully open during the testing and no attempt was made to reduce the pressure of the gas.

Figure 3: Two stage CONCOA hydrogen regulator

2.3 Pre-Hydrogen preliminary instrument testing

Before hydrogen could be put through the system, preliminary tests needed to be conducted to ensure that the components of the system were working correctly. This initial test is used to check that the HPA generates a stable aerosol and to validate the OPC against SI-traceable PSL spheres (NIST Traceable PSL). The initial testing at NPL used a nitrogen pressure of nominally 1 bar and 0.9 µm PSL (0.903 µm ± 0.012 µm). The layout for this system is illustrated in Figure 4.

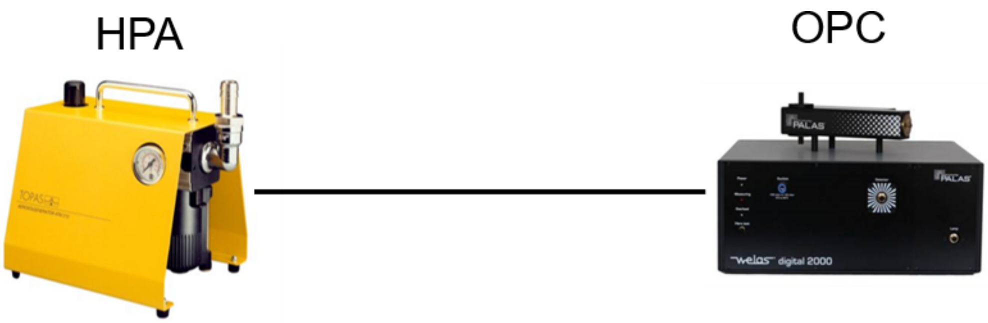

Figure 4: Setup to check the OPC using PSL spheres

As shown in Figure 5 the OPC displayed a maximum particulate concentration at 0.9 µm. This displayed that the HPA could successfully generate a particle laden gas at this size range and that the OPC could successfully detect and size particles from this generation system.

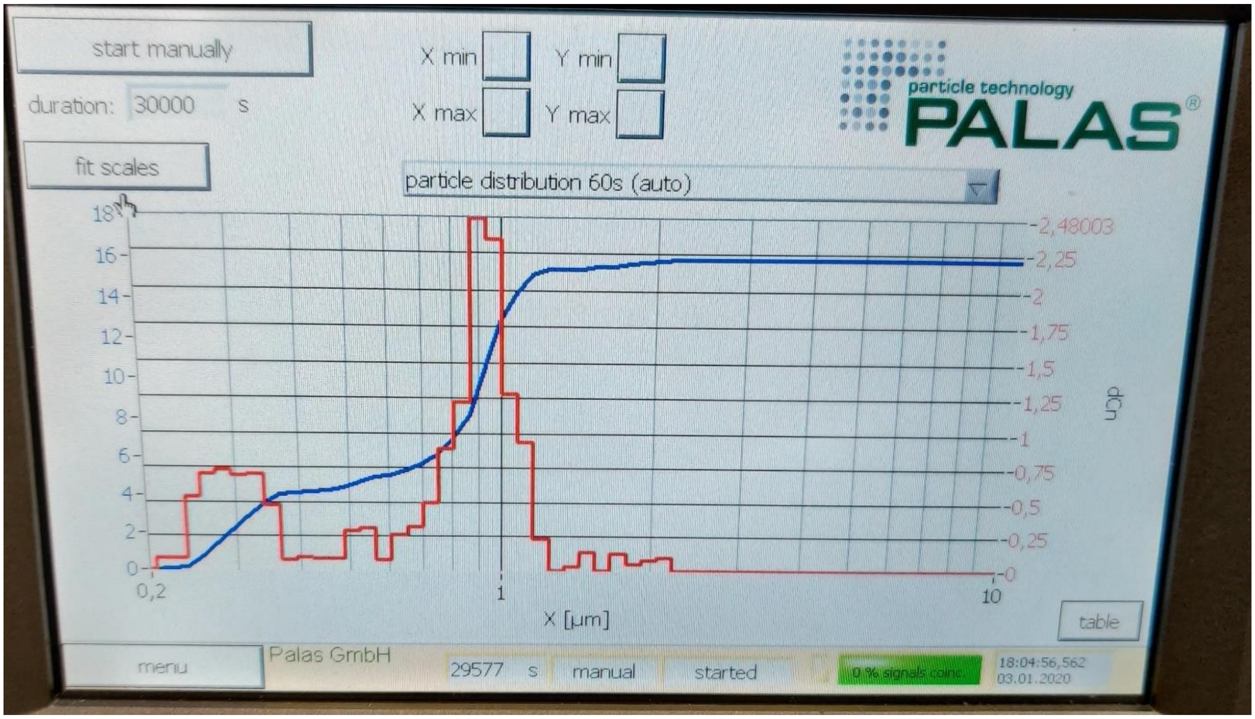

Figure 5: OPC scan of a 0.9 µm PSL aerosol

2.4 Hydrogen sampling system design and procedure

The testing system was setup as shown in Figure 6. Increased pressures, above atmosphere, may be required to aerosolize larger particles; a pressure of approximately 2 bar and a flow of 2 lpm was used during this test. Prior to testing, the system was leak checked. In addition, once the system was constructed, a hydrogen leak detector with a detection range of 1 ppm / 0.1 vol% depending on the display range (Hydrogen Power from Umwelt Sensor Technik) was used to ensure that any significant leaks present during the experiment were swiftly detected. No hydrogen leaks were detected around the OPS connections however a significant leak was detected at the HPA, even after tightening, and so the test was stopped after two personal alarms sounded, signalling a high level of hydrogen in the atmosphere.

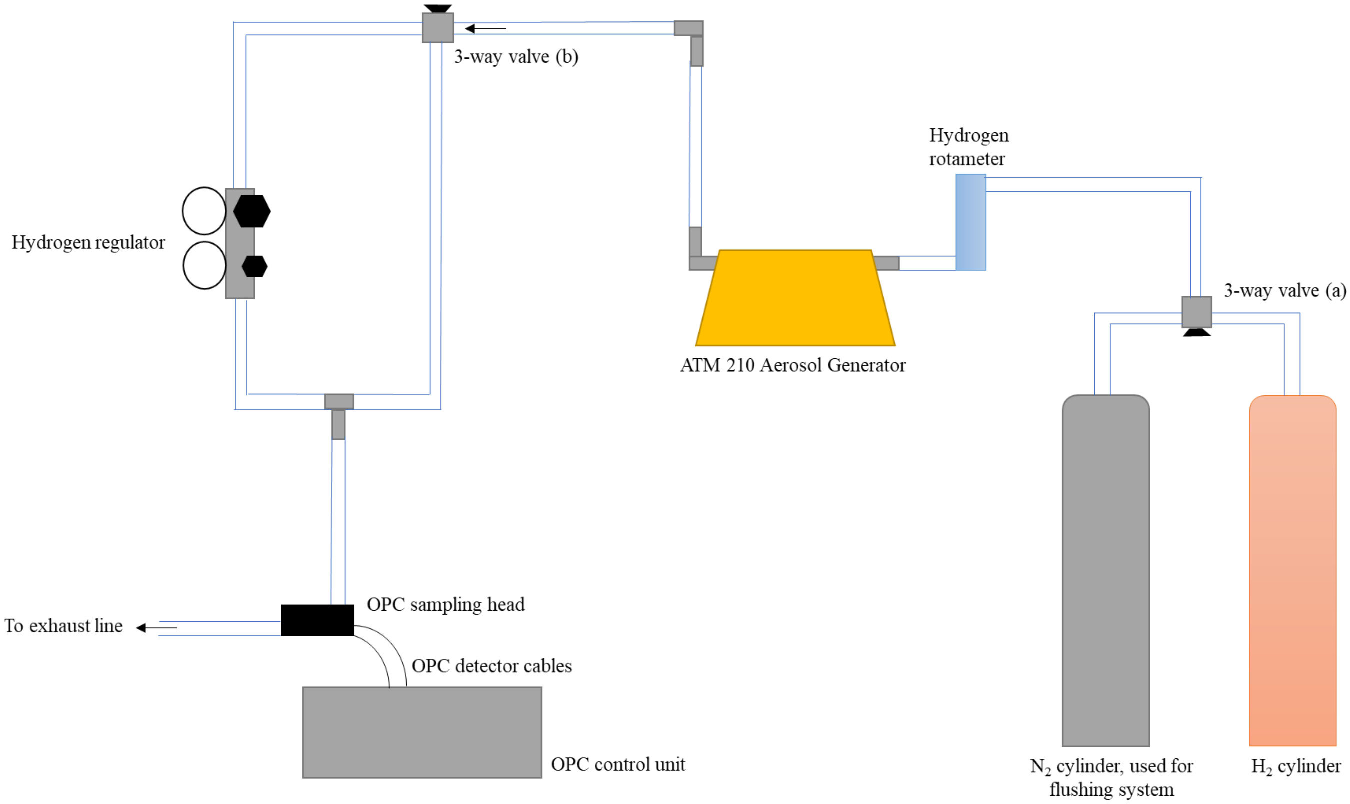

Figure 6: Example setup to determine the particle losses through a sampling system

The procedure was carried out following the series of steps described below:

1. The OPS was positioned in the testing area and powered on, allowing sufficient time for the system to acclimatize and proceed through the standard start-up protocols. The OPC was also set to capture all data from the test, to be saved on the system and to an external USB drive.
2. The sampling system was constructed using stainless-steel tubing and fittings in the above.
3. The relevant regulators were attached to all cylinders and tested for pressure retention.
4. The 900 nm PSLs and deionised water solution was added to the HPA and the system was resealed.
5. Once all connections were sealed, and with three-way valve (a) set to sample from the N_2 cylinder, the cylinder was opened and N_2 gas was passed through the system at a flow rate of approximately 2 lpm and a pressure of approximately 2 bar. The flow was controlled using the rotameter at the front of the HPA.

6. Initially, three-way valve (b) was set to allow the particle laden gas flow through the regulator free side of the system.
7. Once a response was registered on the OPC, three-way valve (b) was switched to allow gas to flow through the regulator. Prior to this, it was ensured that the regulator was fully open.
8. Once a response was registered on the OPC, three-way valve (b) was switched back to sample through the regulator free side of the system.
9. Steps 7 and 8 were then repeated to test the response a second time.
10. After these tests, three-way valve (a) was switched to sample from the H_2 cylinder.

NOTE: At this point, the personal alarms sounded, indicating a hydrogen leak from the system. After tightening all connections, purging the system with N_2, and retrying the test with H_2, the alarms sounded again, and a significant leak was found at the HPA connection, therefore the test was abandoned at this point.

2.5 Determination of losses from a sampling system

The simple equation to determine the losses within a sampling system is very similar to that used in the filter mass determination. By using a 3-way switching valve and identical lengths and diameters of tubing on both branches, we have assured that the only difference between each branch is the sampling system itself. As the generator can be regarded as stable and the OPC is unaffected by sample pressure, the difference in the particle concentration when the 3-way valve is switched will be the losses within the sampling system.

$$\boldsymbol{PL = p_{clear} - p_{system}}$$

where:

PL	=	Particulate concentration loss within the sampling system
P_{clear}	=	Particle concentration at the OPC down the clear branch
P_{system}	=	Particle concentration at the OPC down the System branch

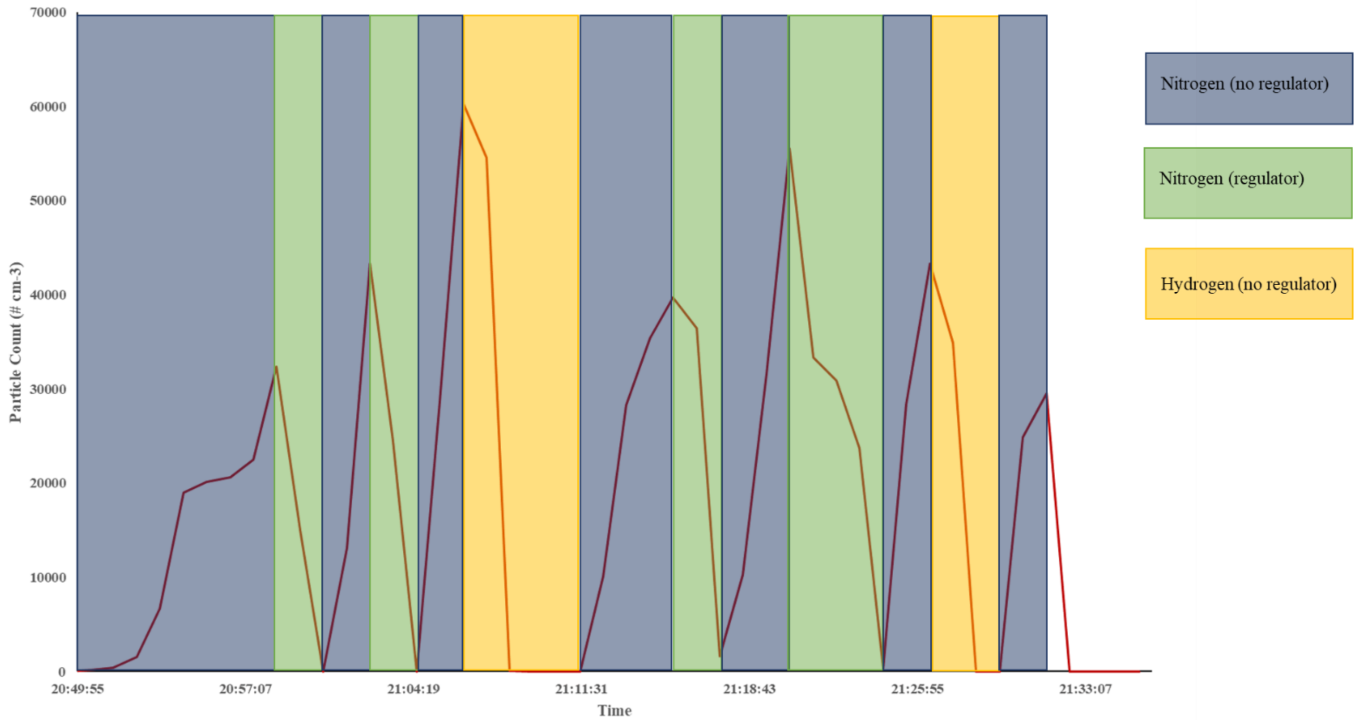

Figure 7: Timeline of results from particle loss testing

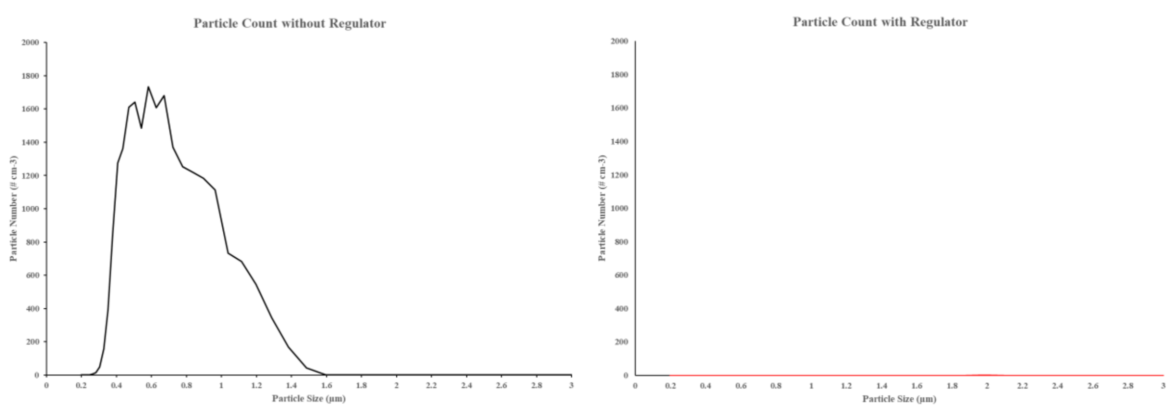

Figure 8: OPC size distributions in nitrogen without a regulator (left) and with a regulator (right)

The testing timeline is split into three different stages; i) nitrogen (no regulator), ii) nitrogen (regulator), and iii) hydrogen (no regulator). The hydrogen testing with the regulator was not carried out on this occasion as the concentration of particles observed in hydrogen without the regulator was nominally 0 cm^{-3}, and the personal alarms detected hydrogen leaks in the system. The hydrogen was tested twice, but on both occasions the personal alarms sounded, therefore the test was terminated.

As can be seen in Figure 7 and Figure 8, a particle loss of > 95% was recorded when the carrier gas stream was switched from the path with no regulator to the path with the regulator. As noted, this test was only carried out using nitrogen as the carrier gas. When the carrier gas was switched from nitrogen to hydrogen on the unregulated side of the system, particle losses of > 99% were recorded on both occasions. Owing to the complete loss of particles when switching to hydrogen, and the sounding of the personal alarms, the hydrogen was not passed through the regulator system.

3 Conclusions

This Good Practice Guide is intended to be used as helpful document to support accurate sampling from the hydrogen refuelling station and understand whether it was feasible to regulate pressure without affecting particulate mass concentration.

PSA-H70 from HYDAC was the only filter sampling instrument available at the time of testing; it enables particulate filter sampling without the use of a pressure regulator. In line with the objectives set out in the EMPIR MetroHyVe project, this guide has highlighted the initial considerations for using an HPA for the generation of a particle laden gas and an OPC instrument for in-line sampling of particulate contaminants in a hydrogen gas stream. It has been demonstrated that in a nitrogen carrier gas all the 900 nm particles were lost before they reached the detector. This highlights potentially serious issues with using a regulator in a particulate monitoring system.

Further testing of the system would be required in order to resolve the issues identified during the experiment, namely the identified hydrogen leaks, which originated from the HPA system.
Due to the restrictions in place relating to the current COVID-19 crisis, it was not possible to test this system for an extended period, or at a hydrogen refuelling station.

4 Recommendations

- The use of a high-pressure filter system such as the PSA – H70 is recommended for sampling from refuelling stations during the filling process.

- The use of a pressure regulator during particulate measurements is not recommended due to potential particulate losses.

- The use of a system similar to that used in this study would be recommended to determine particulate losses in a sampling system, although extra care should be taken to eliminate hydrogen leaks in any particulate generation system such as a HPA.

4 – References

[1] PALAS particle technology, "Operation Manual Light-scattering spectrometer, Promo® 2000", version V001032010, 2010.

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[7] A. Murugan *et al.,* "Measurement challenges for hydrogen vehicles," *Int. J. Hyd. Ene*., vol. 44, pp. 19326 – 19333, 2019.

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