METROLOGY for HYDROGEN VEHICLES

REPORT:

A4.2.1: A review of existing particulate sampling techniques at hydrogen refueling stations

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www.metrohyve.eu

This report was written as part of activity A4.2.1 from the EMPIR Metrology for Hydrogen Vehicles (MetroHyVe) project. The three year European project commenced on 1st June 2017 and focused on providing solutions to four measurement challenges faced by the hydrogen industry (flow metering, quality assurance, quality control and sampling). For more details about this project please visit www.metrohyve.eu.

This guide was written by:

Jordan Tompkins National Physical Laboratory *www.npl.co.uk*

Contents

Introduction

In hydrogen fuel cells, it is imperative that the hydrogen is clean/pure as certain impurities can reduce the lifetime and efficiency of the fuel cell within the vehicle. ISO 14687-2 includes a threshold for particle mass concentration at 1 mg kg^{-1} for hydrogen provided to full cell vehicles. The current method used for measuring particles in hydrogen is by placing particulate filters in the stream of supplied hydrogen and weighing the filters before and after mass is collected.

Table 1 — Directory of limiting characteristics

Characteristics (assay)	Type I, Type II Grade D
Hydrogen fuel index (minimum mole fraction)[a]	99,97 %
Total non-hydrogen gases	300 µmol/mol
Maximum concentration of individual contaminants	
Water (H_2O)	5 µmol/mol
Total hydrocarbons[b] (Methane basis)	2 µmol/mol
Oxygen (O_2)	5 µmol/mol
Helium (He)	300 µmol/mol
Total Nitrogen (N_2) and Argon (Ar)[b]	100 µmol/mol
Carbon dioxide (CO_2)	2 µmol/mol
Carbon monoxide (CO)	0,2 µmol/mol
Total sulfur compounds[c] (H_2S basis)	0,004 µmol/mol
Formaldehyde (HCHO)	0,01 µmol/mol
Formic acid (HCOOH)	0,2 µmol/mol
Ammonia (NH_3)	0,1 µmol/mol
Total halogenated compounds[d] (Halogenate ion basis)	0,05 µmol/mol
Maximum particulates concentration	1 mg/kg

For the constituents that are additive, such as total hydrocarbons and total sulfur compounds, the sum of the constituents are to be less than or equal to the acceptable limit.

[a] The hydrogen fuel index is determined by subtracting the "total non-hydrogen gases" in this table, expressed in mole percent, from 100 mole percent.

[b] Total hydrocarbons include oxygenated organic species. Total hydrocarbons shall be measured on a carbon basis (µmolC/mol). Total hydrocarbons may exceed 2 µmol/mol due only to the presence of methane, in which case the summation of methane, nitrogen and argon shall not exceed 100 µmol/mol.

[c] As a minimum, total sulphur compounds include H_2S, COS, CS_2 and mercaptans, which are typically found in natural gas.

[d] Total halogenated compounds include, for example, hydrogen bromide (HBr), hydrogen chloride (HCl), chlorine (Cl2), and organic halides (R-X).

Table 1: ISO 14687-2 Technical Specifications For Hydrogen Purity

A literature review was conducted to determine the state of the art for sampling devices in this area.

Available Devices

An extensive review of commercially available particle sampling devices was carried out. Only a single device was identified for particle sampling at 700 bar in hydrogen, the Hydac and Wenger Engineering's Particle Sampling Adapter-H70 (PSA-H70).

Figure 1: PSA-H70

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".

Instrument Operation

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.

Technical Specifications

- Nominal Size: DN04
- Nominal Pressure: PN800
- Flow Rate: 60 g/sec
- Medium: Hydrogen H2 (Gas)
- Temperature
  - Medium: -40˚C to +80’C
  - Ambient: -20’C to +50’C
- Weight: 16kg
- Filtration Rating: 5µm

Support Grid: 150µm

Availability and Impact

Wegner Engineering, co-creator of the PSA-H70, details the specifications on their website and offer information through their sales department. Hydac, as well as selling it, offer cleaning and analysis services for the product. Hannovermesse also displays and sells the product at their exhibitions and Newsmax, a Dutch science news website, explains the sampler.

The PSA-H70 has been used in the HyCoRA project; a project aiming to provide information to reduce cost of hydrogen fuel Quality Assurance. Three sampling campaigns were conducted in HyCoRA, in late 2014, summer 2016 and spring 2017. Unique data set, a total of 28 gas samples and 14 particulate samples, has been sampled, analysed in compliance with ISO 14687/SAE J2719 and disseminated. The first campaign concentrated on feedstock and the second addressed newly commissioned stations. Simultaneous collection of gas and particulate samples lead to challenges, and should be validated further. When sampling was performed after gas sampling, no particles were found. However, if the particles were collected before the gas sampler, uncertainties around introduction of small levels of impurities into the hydrogen would become a concern. The PSA-H70 has also been used by the Japanese Industrial Standard (JIS); Japan's national standardization body.

The device is available at a price of nominally £16K. A second generation instrument is now being sold which appears to have been adapted for ease of use.

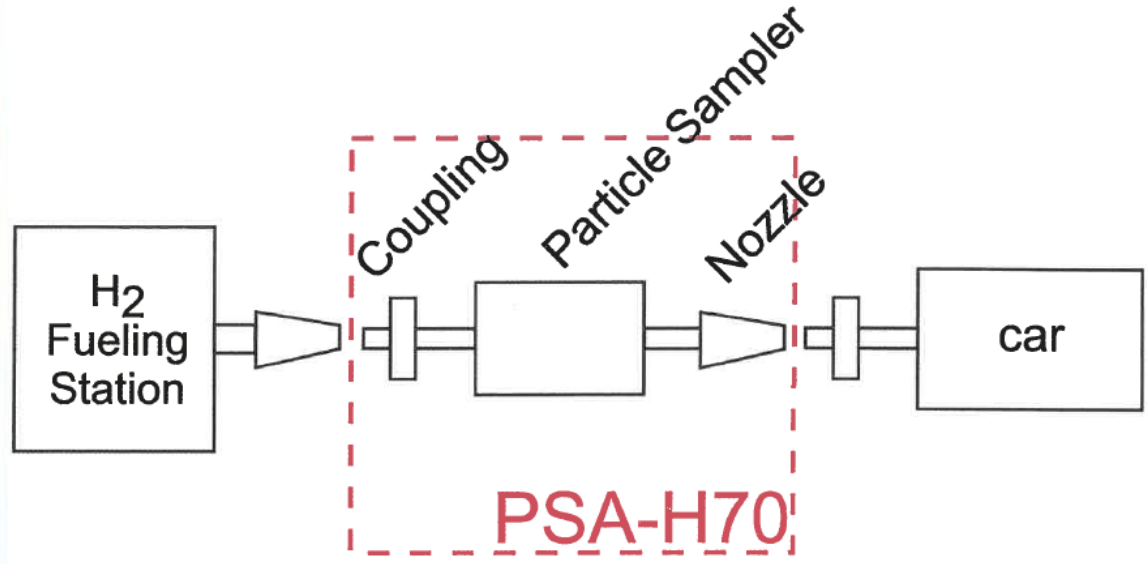

Figure 2: Positioning of the PSA-H70 in the HRS

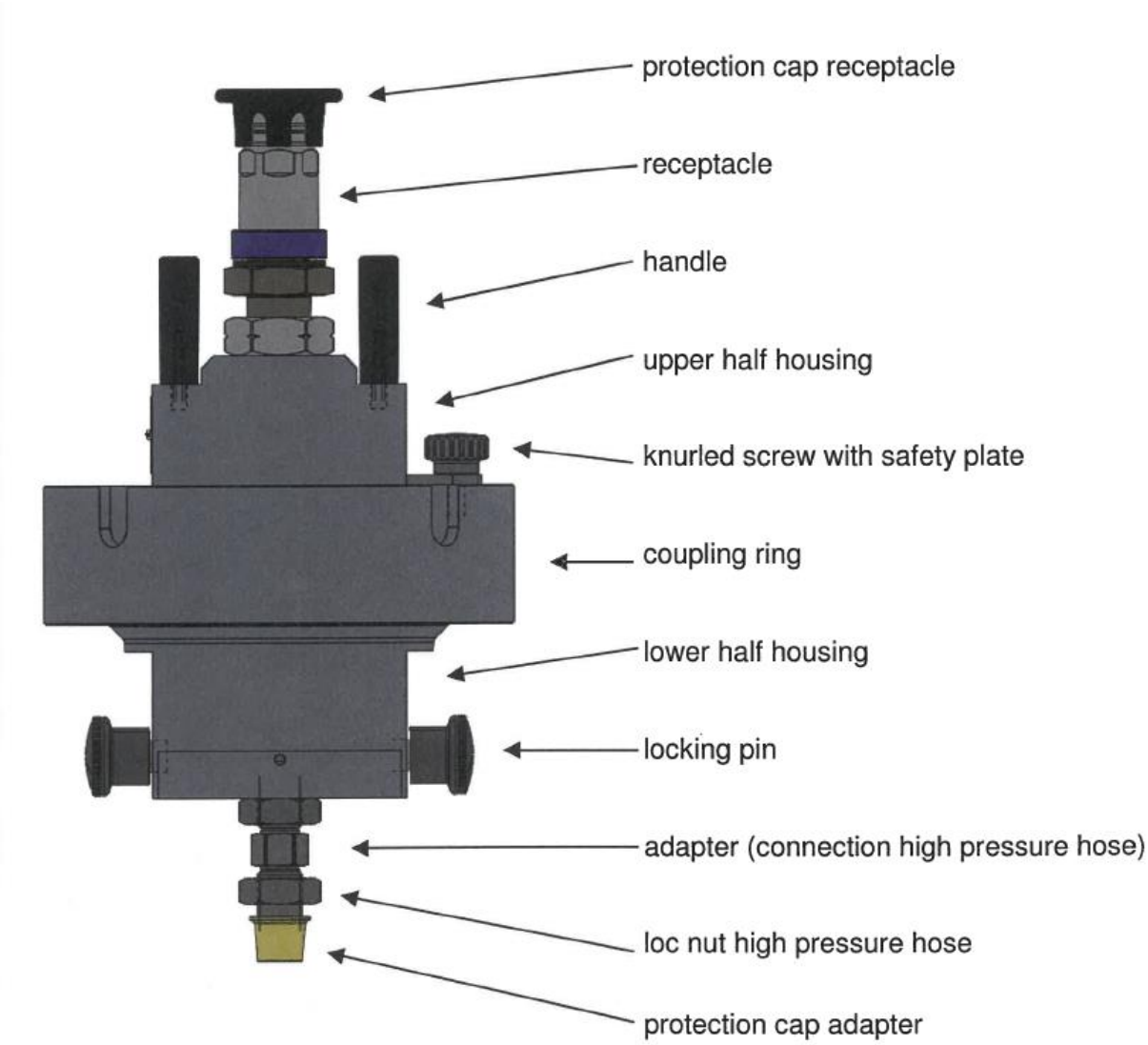

Figure 3: Schematic of second generation PSA-H70

The PSA-H70 has an inbuilt bypass system so that the initial gas pulse from the HRS is diverted away from the filter so as not to damage the filter membrane.

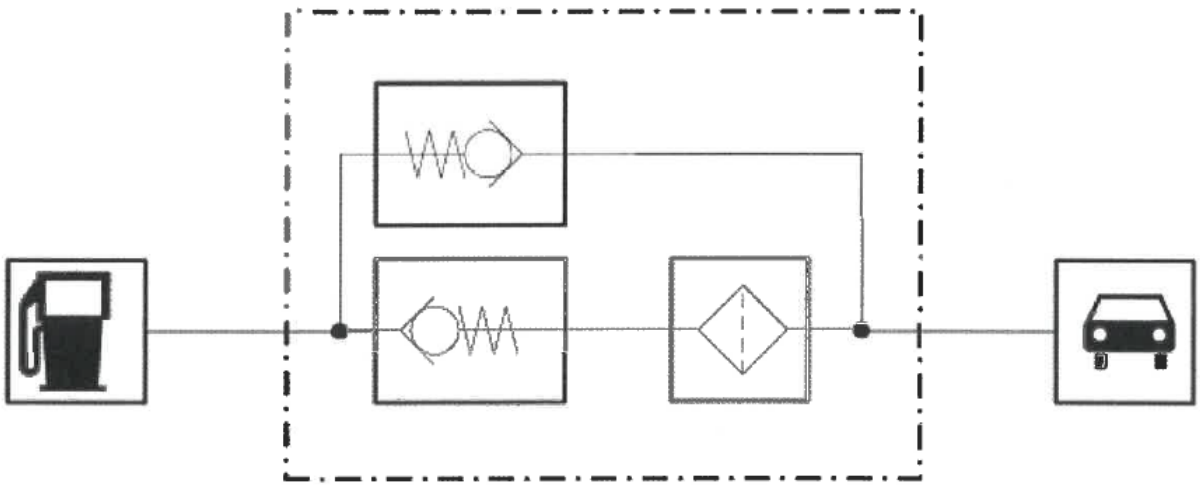

Figure 4: Filter bypass schematic

Specific filters are required for use in the PSA-H70 due to the high pressures involved and also the force with which the filter must be clamped down into the device. Fibrous filters can be damaged by this process.

Figure 5: Filter

Conclusion

Hydrogen sampling at high pressures (700 bar) is a new scientific issue due to the introduction of hydrogen refuelling stations. Currently there only appears to be one device that is commercially available. As the PSA-H70 is a relatively new piece of equipment there are currently not many suppliers or studies into its usage and performance. Therefore, the MetroHyVe project will select this device for the sampling campaign, but will verify its performance in a separate activity in comparison to online techniques (A 3.3.3). It looks as though the PSA-H70 is undergoing constant improvement as a second generation model came out during the creation of this report. As the only device available to allow the measurement of particulate mass concentrations without the use of a pressure regulator this is extremely important for the hydrogen sampling area and the industry as a whole.

Although there is nothing stated in ISO 14687-2 about a recommended filter pore size, it would be better to look at using filters closer to the 0.3 micron size, which are used routinely in the air quality area. These filters have been shown to successfully trap particles down to 4 nm and would help to ensure that no particles are being transported through to the fuel cell. If the issue is potentially oil mist then filters of 0.3 micron pore size would allow for greater confidence in a ‘zero’ reading during a particulate measurement. NPL will be looking at using such filters in future testing in the MetroHyVe project.