METROLOGY for HYDROGEN VEHICLES 2

Good Practice Guide

Good practice guide for representative sampling and analysis of particulate matter in hydrogen fuel dispensed from hydrogen refuelling stations

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Good Practice Guide	
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Summary

This document summarizes state-of-the art for sampling of particulates from hydrogen fuel. The most recent scientific documentation for sampling is reviewed, including updated standards like ASTM D7650, ISO 19880-1 Annex K. The information is compared with the D3 Good practice guide for the handling, transporting and weighing of filters from particulate sampling in gaseous hydrogen published by MetroHyVe 1 project.

Confidentiality	Public

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Introduction

This report was written as part of activity 3.3.1 from the EMPIR Metrology for Hydrogen Vehicles 2 (MetroHyVe 2) project. The three-year European project commenced on 1st August 2020 and focused on providing solutions to four measurement challenges faced by the hydrogen industry (flow metering, quality assurance, quality control and sampling). For more details about this project please visit https://www.sintef.no/projectweb/metrohyve-2/.

Task objectives under MetroHyVe 2

SINTEF with the support of ITM Power, NPL and ENGIE will review the state of the art of particulate sampling with emphasis on the filter thickness, filter type, pore size (HYDAC, ASTM recommendation or standard) and available results and experience obtained on it. The review will update the good practice guide for particulate sampling delivered by MetroHyVe 1.

Scope of the Good Practice Guide

This document aims to summarize state-of-the art for sampling of particulates from hydrogen fuel. The most recent scientific documentation for sampling is reviewed, including updated standards like ASTM D7650, ISO 19880-1 Annex K. The information is compared with the D3 Good practice guide for the handling, transporting and weighing of filters from particulate sampling in gaseous hydrogen published by MetroHyVe 1 project.

Particulate contamination causes and issues

The concentration of particulate matter in hydrogen fuel is controlled by ISO 14687 to a maximum limit of 1 mg/kg. There are several sources to particulate impurities: production method, fuel transport and hydrogen refuelling station (HRS). Interaction between impurities in the fuel can potentially lead to formation of condensed phase matter like acids or salts. For carbonaceous feedstocks (e.g. biomass) tar formation could source particulate materials in the fuel (Nikolaidis & Poullikkas, 2017). HRS is itself a potential source of particulate matter with potential contributions from stainless steel piping. For fuel cell vehicles, and in-line filter of 10 µm is used to restrict large particles from interaction with fuel cell system components. Still, smaller particles could have a negative impact and control must ensure concentration to be lower than 1 mg/kg.

Sampling of particulates in hydrogen fuel

The report will first present the different particulate sampling system that can be used at HRS and their requirements and operations. The report focusses on standardised test method (reported in international standard) or commercial systems (i.e. HYDAC, Airborne Laboratory). Then a review of the different filter types used or recommended will be provided.

Particulate sampling system

Standardised test method according to ASTM D7650-21 (draft 2020/11)

The standard practice is primarily for sampling of particulates in hydrogen fuel used for fuel cell vehicles, internal combustion engine vehicles or other gaseous fuels up to a nominal working pressure of 70 MPa using an in-stream filter. The test method describes a sampling apparatus design, operating procedures required to obtain the stated levels of precision and accuracy. In 2020, the ASTM D7650-13 is currently being revised by the D03.14 subcommittee.

Apparatus design

The apparatus design must be compliant with the maximum allowable working pressure of the HRS dispenser. Full flow is stated as a requirement for a representative sample to be collected, in addition to a sampled mass of more than two kilograms. All apparatus must be constructed with materials compatible with the fuel being sampled and must withstand temperatures between -40 °C and 85 °C. A pressure relief valve meeting the requirements of ASME BPVC (boiler & pressure vessel code) shall be installed. For safety, anti-whips and grounding wire shall be installed.

It is recommended to add a rotary ball valve, ball valve, or needle valve before the filter housing to prevent the high-pressure test pulse from rupturing the filter. The receptacles shall be designed in accordance with SAE J2600 for hydrogen. The receptacle used shall not contained a particulate filter.

Filter housing requirements

An example of a filter housing is shown in Figure 1. The general construction is to have a filter installed on a support. Inner and outer O-rings are used to seal the housing when assembled. Assembly can be done with either housing screws or a combination of internal and external threads to the housing inlet and outlet plates.

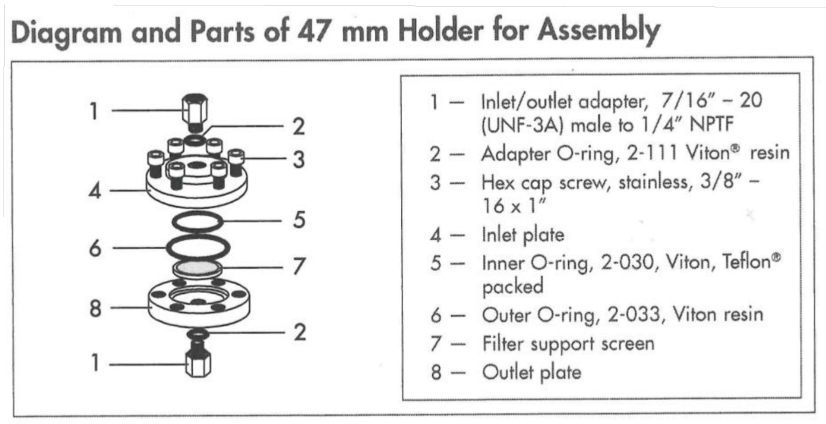


Figure 1. Diagram of example filter holder. Illustration by Airborne Laboratories.

Exhaust line requirements

The procedure describes three options for venting of the sampled fuel:

1. A tank vent system, where the tank shall meet the requirements of SAE J2579 or UN GTR 13.
2. Atmospheric vent system where the outlet should be at a minimum of 2.4 meters above the ground and be placed clear of canopies that may trap hydrogen gas.
3. Vehicle vent system comprising a high-pressure hose and nozzle for connection to a FCEV receptacle.

A high-pressure hose with appropriate rating should be connected from the filter assembly to the outlet adapter.

Metering of the dispensed fuel

Depending on the venting strategy chosen, there are three options available for estimating the dispensed fuel:

1. Measurement of the temperature and pressure of the tank vent system, it allows to calculate the dispensed volume.
2. Measurement of the flow using Coriolis mass flow meter calibrated for the appropriate gas flow and with a totalizer to calculate the mass of fuel sampled.
3. Recording of the HRS dispenser meter, it can only be used when using FCV as sink.

Standardised test method according to ISO 19880-1 Annex K

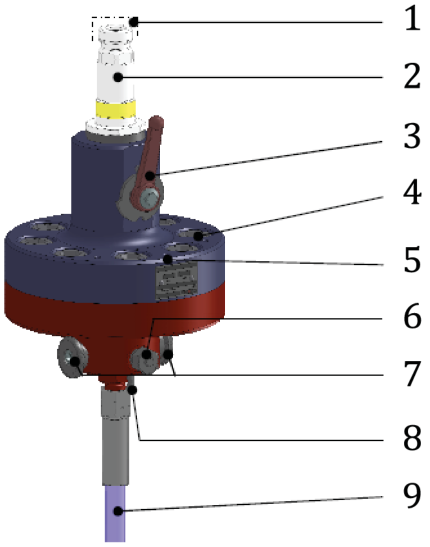
Annex K was written at a time when the HYDAC PSA-H70 was the only available commercial sampling adapter on the market.

Particle sampling instrumentation description

The hydrogen particulate sampler adapter (HPSA) is a high-pressure filter holder to be placed in between the dispenser nozzle and the FCEV receptacle. The dispenser nozzle connects on the top of the sampler whereas the bottom end is connected to the FCEV through a high-pressure hose and a 70 MPa hydrogen nozzle. A bleed valve allows for purging of the instrument prior to sampling as well as depressurization after sampling is finished.

In order to prevent the 87,5 MPa pressure test pulse from rupturing the filter, a rotary valve is used to limit the pressure prior to sampling. Alternatively, a ball valve or needle valve could be used to initially reduce the force acting on the filter. Full flow and pressure are required in order to have a representative particulate concentration collected onto the filter.

Depressurization of the HPSA adapter is required before disconnecting it from the FCEV. In order to avoid venting of hydrogen through the bleed valve, an alternate configuration is possible: by tubing the HPSA vent system to a T inserted between the dispenser nozzle and the HPSA receptacle. With the HPSA check valve located downstream the tee, the HPSA could effectively be vented with the depressurization of the dispenser hose and nozzle. See Figure 2 and Figure 3 below.



1	protective cap	6	bleed valve
2	receptacle	7	fixing plate for containment grip (×2)
3	rotary valve	8	vent nozzle
4	housing screws (×8)	9	high pressure hydrogen hose
5	grounding point for potential equalisation		

Figure 2. Particulate sampling adadpter, HYDAC PSA-H70 shown.

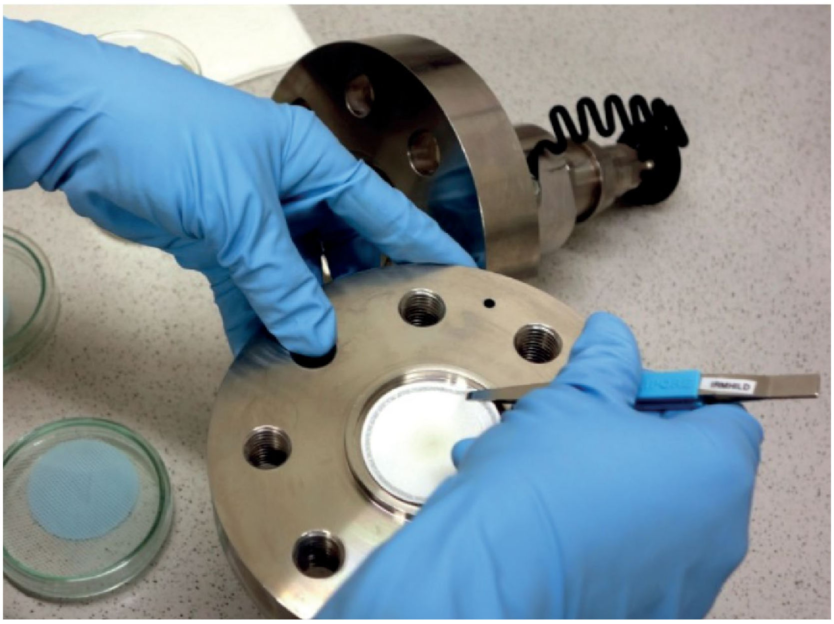


Figure 3. Micron filter element removal from hydrogen particle sampling adapter unit.

The HYDAC Operating Manual (HYDAC, Operating manual, 2013) lists both 0.2 µm and 5 µm filters as options to be used with the PSA-H70 adapter: Millipore PTFE Porex B 5 µm, Ø 47.0 mm or Filter membrane ALBET Lab Science PTFE hydrophob blanca 0.2 µm, Ø 47.0 mm, PT 020 47 BL.

HYDAC system MK2 (commercially available in 2020)

HYDAC revised the PSA-H70 in a MCP 02 version released in 2018. The main difference is in the design of a feedback loop, allowing the adapter to be depressurized through the HRS nozzle instead of by the use of a bleed valve. The principle is illustrated in Figure 4.

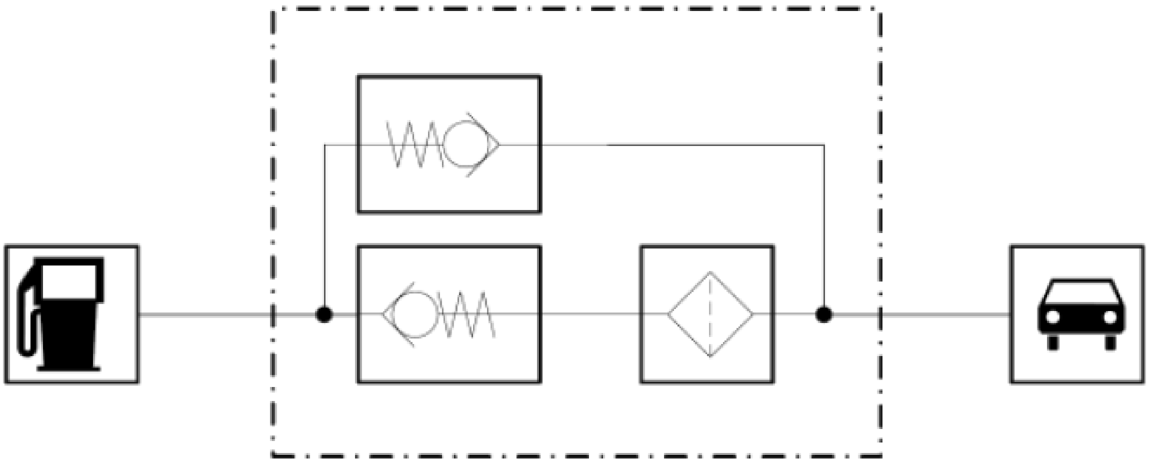


Figure 4. HYDAC MCP 02 PSA-H70 depressurization loop.

The rotary ball valve has also been removed. According to HYDAC, the pressure pulse degrades the filter support but does not rupture the filter. Therefore, filter supports are now replaced between every sample collected.

The MCP further changes the design by replacing screws with inner and outer threads. An open-jaw torque wrench is used for assembly of the adapter. The adapter is illustrated in Figure 5.

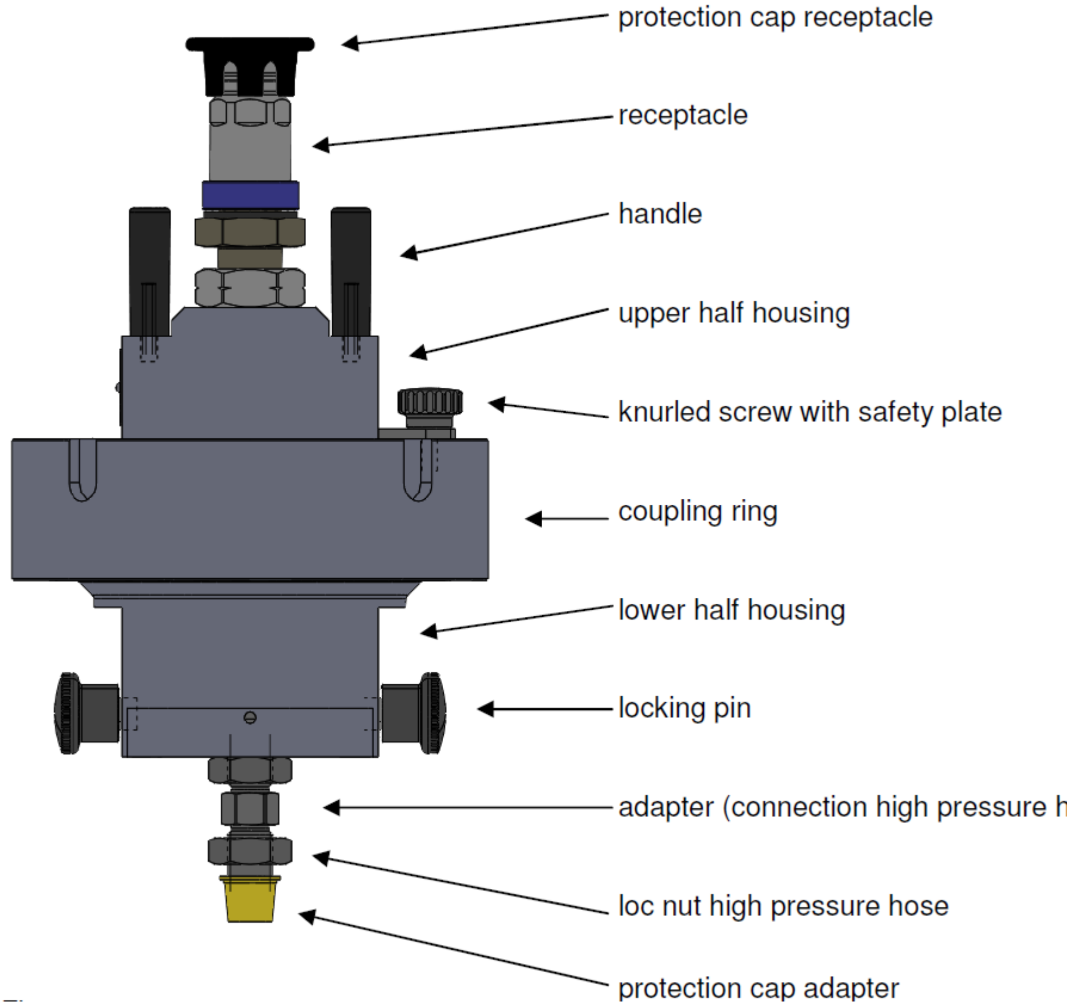


Figure 5. MCP 02 PSA-H70.

The HYDAC Operating Manual lists a 5 µm filter (Millipore hydrophobic PTFE 5.0 µm, diameter 47 mm, Product reference: Millipore Mitex LSWP04700) as recommended filter to be used with the PSA-H70 adapter:.

The HYDAC PSA-H70 adapters in both versions does not have a safety relief valve as suggested by ASTM D7650.

Airborne Laboratories MRM-7650 (commercially available in 2020)

Airborne laboratories offer a commercial implementation of ASTM D7650. The instrument is rated at 137 MPa (20,000 psi) and is designed for flow rates up to 125 g/s. It includes an inlet 2-way ball valve as well as a pressure relief valve. The instrument is designed for atmospheric venting of hydrogen. The filter housing (Figure 1) can be replaced so that the adapter can be used for several sampling campaigns with the option of using several filter housings.

Figure 6. AirborneLabs MRM-7650.

Since the MRM-7650 uses atmospheric venting, a Coriolis flow meter with totalizer is used to estimate the total mass of hydrogen passed through the adapter. A schematic of the MRM-7650 is shown in Figure 7.

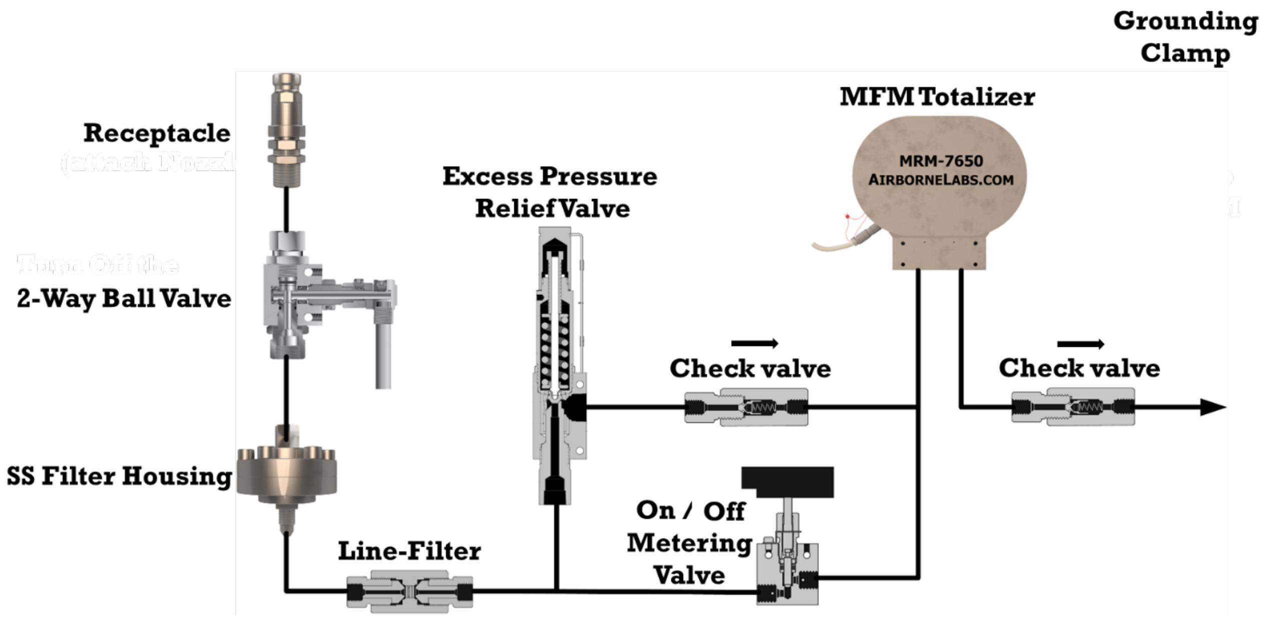


Figure 7. Schematic of the MRM-7650.

Measurement parameters influencing particulate sampling

Several studies have been performed on the recent years around parameters that could influence the particulate sampling as pressure regulator or sampling flow rate. This section will provide a summary on these parameters.

Losses of particulates over pressure regulators

In MetroHyVe, particulates losses over pressure regulators has been extensively studied (Tompkins & Buckley, 2020). By using a particle generator at high pressure (high pressure atomizer) – as well as a optical particle counter it was possible to show that for a 900 nm particle stream, all particles were lost when applying a pressure regulator. The recommendation from the Good Practice Guide was to avoid the use of pressure regulators when sampling particulates from a hydrogen stream.

Dependence on sampling on the flow rate

Early work from California (Birdsall, 2008) indicated that the flow rate has an impact on particulate size. Figure 8 illustrates the impact on four size fractions, where the impact of flow is larger for larger particles.

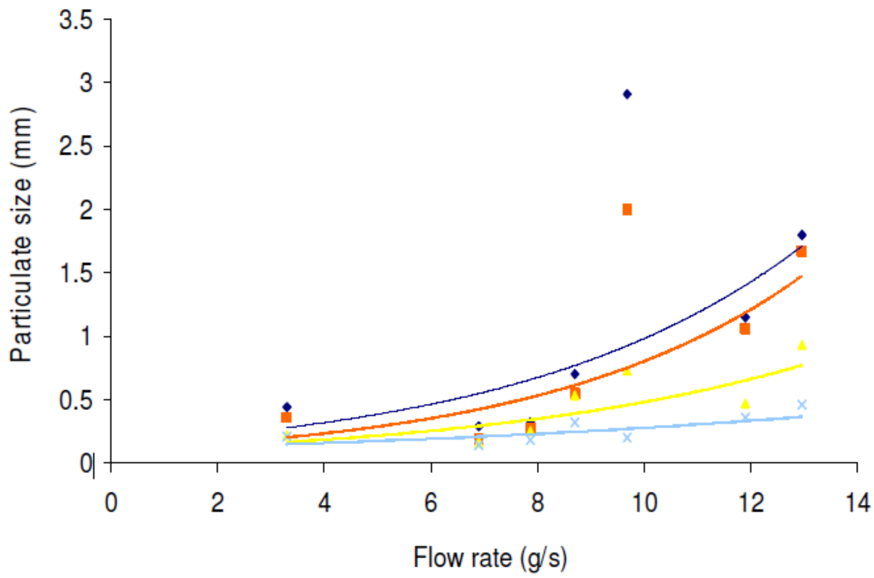


Figure 8. Flow rate impact on particulate size sampled.

For HYDAC sampling with FCV as sink, 60 g/s representative flow is obtained. Also, when using a tank as sink, this can be obtained. However, when using venting to air it is not advisable to perform venting at pressures higher than 35 MPa. The difference between 35 MPa and 70 MPa has yet to be tested.

Selection and analysis of filters for particulate

This section will present the different types of filter that may be used for particulate sampling in hydrogen. Then a review of the gravimetric method to determine the amount of particulate on a filter will be done using standardised method (ASTM D7651-10), instrument manufacturer protocol and EU project good practice guide (MetroHyVe Deliverable 3). Finally filter visual inspection will presented with the benefit of this approach in correlation to gravimetric determination.

Filter types

Several filter types are recommended by the different instrument manufacturer and providers.

A 47mm diameter polytetrafluoroethylene (PTFE) filter (PTFE Membrane Disc Filters). For example, a Pall TF-200 47mm 0.2 µm (P/N 66143) with a pore size of 0.2 µm, as described in ASTM D7650-2013, has been used. This type filter has two sides: one is PTFE and the other is polypropylene. Only the PTFE side faces incoming hydrogen fuel and collects particulates in hydrogen.

Table 1. Filter parameters used for particulate sampling

Filter reference	**Filter type**	**Pore size**	**thickness**	**Equipment or method use**	**Comment**
Pall TF-200 47mm	PTFE Membrane Disc Filters	0.2 µm	139 µm	ASTM D7650-13 MRM-7650	Filter has two sides
Millipore Mitex LSWP04700	hydrophobic PTFE	5.0 µm	170 µm	HYDAC PSA70 MK2	Unable to be used in autohandler
Millipore PTFE Porex B 5 µm, Ø 47.0 mm	PTFE	5.0 µm	n.a.	HYDAC PSA70	Not commercially available in 2020
HahneMuhle PT 020 47 BL	PTFE reinforced by a Polypropylene net	0.2 µm	unknown	HYDAC PSA70	

Several filters type (pure quartz, fibrous and porous PTFE filters) were evaluated for hydrogen application in MetroHyVe Deliverable 3 report. Quartz filter (Pallflex® Tissuquartz™ Air Monitoring Filters - 47 mm Product ID 7202) are brittle and can shed fibres. It was found that PTFE Coated Boro Silicate Glass Fiber Substrate (MTL GP47DMCAN) swelled in hydrogen and curling of the filters were observed. Porous filters (Millipore Mitex LSWP04700) did not behave this way and were thus recommended for this application. Another PTFE film filter was evaluated (MTL PT47P) but were not able to handle high pressure. It has been used for low pressure sampling at few bar.

New filters must be demonstrated to be particle free. Filters must be inspected and conditioned before use. Inspection and conditioning must be performed in a temperature and humidity-controlled environment free of particulate matter.

Gravimetric analysis of filters

References to descriptive methodology for gravimetric analysis is given in the following. It should be noted that these references do not discuss some of the practical challenges associated with gravimetric analysis, namely that filters may curl up with changing temperature and relative humidity.

ASTM D7651-10

ASTM D7651-10 (ASTM, 2010) defines the test method for gravimetric analysis of the particulate filters. Important details from the method are referenced here.

Filter handling

Filter should be at all times handled with powder-free gloves. Filter equilibration for at least 24 hours in controlled (i.e., temperature and moisture) environment is prescribed. US EPA conditions for PM10 samples are given as example: 25 °C and 20-30 % RH.

Balance

The balance used should provide a 10 µg resolution and should be calibrated with NIST traceable standards (± 0.1 mg). Here, 0.05 and 0.2 g are given as examples of traceable standards. The balance should be placed in a controlled atmosphere.

Glove box

A glove box is typically used to provide a controlled atmosphere for the balance. A clean atmosphere with RH < 30 % is typically provided with nitrogen gas. A static charge removal device is required in order to prevent charging and potential loss and agglomeration of particulate matter.

Data logging

Data logging for both the glove box controlled atmosphere as well as balance is advised for reference and the possibility to infer sample mass stability.

Method precision and bias

Whereas terminology is defined in the method, performance data is not given.

HYDAC MCP 02 PSA-H70 Operations manual

The Operations manual (HYDAC, MCP 02 PSA-H70 Operations manual, 2018) for the MCP 02 PSA-H70 sampling adapter has a section dedicated to laboratory analysis of the filters used to collect particulates. The manual gives general reference to ASTM D7651-10, however the manual differs from said methodology on a number of points.

Negative control value

The negative control value represents the total mass from interference. For estimation of the negative control value it is referred to ISO 16232.

Clean room requirements

The document gives reference to a Class 7 clean room requirement which is interpreted to refer to ISO 14644-1:2015 class 7. This implies that the clean room atmosphere must contain no more than 352 000 particles > 0.5 micron per cubic meter and 60 HEPA filtered atmosphere changes per hour.

Visual inspection of filter and filter support

The filter and the filter support integrities are visually inspected, and their integrity checked. For particulate size determination for material collected on the filter, it is referred to ISO 16232.

Determination of chemical impurities

In order to qualify and quantify chemical impurities a high-purity solvent is used to dissolve impurities from filter and filter support. Chemical analysis is performed according to the impurities collected.

Gravimetric analysis

Conditioning of the filter and filter support are to be conducted in a drying oven at 85 °C for approximately 45 minutes before cooling for an additional 30 minutes in an exicator.

Balance

A requirement of a resolution of 300 µg is stated.

Cleaning of the sampling adapter

The sampling adapter is cleaned with a high purity solvent. Heptane (p.a. 99.99 %) was mentioned as an alternative. The solvent needs to be filtered through a 0.2 µm filter prior to use. Chemical analysis of the solvent is used to establish a blank value used as contrast to the value obtained in a similar manner after sampling has been conducted.

MetroHyVe D3 Good practice guide for the handling, transporting and weighing of filters from particulate sampling in gaseous hydrogen

This Good Practice Guide (Thompkins, 2020) aspires to document at traceable, gravimetric method for particulate laden filters used for quality control of hydrogen fuel. Type of filter, effect of ambient conditions on the filter is addressed.

Method

The method is applicable to collection of masses between 25 µg and 8 mg, with a maximum mass of filter and collected particulates of 300 mg.

Sample storage

In order to avoid evaporation, filter should be store at a temperature below 23 °C. A storage life of the filters of 2 months has been indicated. It has also been informed from NPL side that filters are now stored in a fridge at 4 °C in order to minimize loss of volatile compounds.

Balance

A balance with a resolution of 0.1 µg was specified. For PTFE filter a faraday cage pan is prescribed.

Autohandler

A filter autohandler with an atmosphere of 20 °C ± 1 °C and 47.5 ± 2.5 RH % can be used. Clean room forecourt was not deemed necessary when handling filters.

It has also been informed from NPL that several filter types were not suitable for autohandler as Millipore Mitex due to slight curviness of the filters. These filters will require manual weighing.

Measurement uncertainty for handling filters in forecourt without cleanroom was estimated to be 17 µg.

Gravimetric analysis

A comprehensive guide to the gravimetric analysis sequence were given in the document, including both intermittent analysis of reference materials and repeated analysis in order to minimize error.

Uncertainty budget

A table with relevant contributions to uncertainty was given. These include effect of humidity on filter, effect of filter drift, effect of humidity on particulate and loss of volatiles. Combined standard uncertainty of 85.6 µg was estimated.

With reference to ISO 12341 (ISO, 2014), there is a limit for 40 µg and 60 µg in mass difference within a 24-hour period for sampled and unsampled filters respectively.

Blanks

Both weighing room and field blanks were used for accounting of conditions in the weighing room and impact on field conditions on the filter itself.

Visual inspection of filters

Although gravimetric analysis is the only requirement set by 14687:2019, visual inspection of filters can provide information about particulate size but also deposition of liquid onto the filter. An example for H2MovesScandinavia project (Aarhaug & Ferber, 2013) is shown in Figure 8.

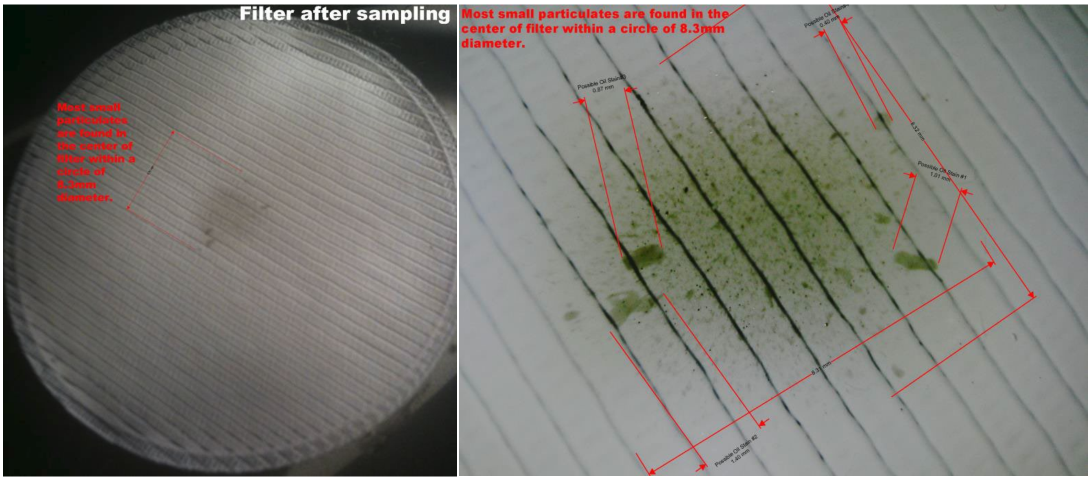
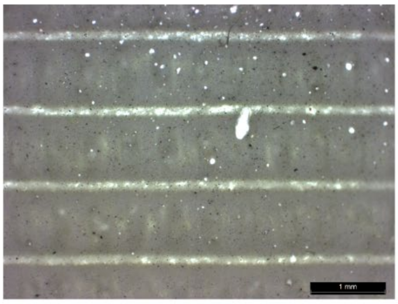


Figure 9. Optical microscope inspection of filter. Picture to the right is magnified 27 times and identifies green, oily residue. Four large spots of diameters 1.4, 1.0, 0.87 and 0.40 mm. 48 particulates of diameter larger than 0.02 mm were found in the 8.3 mm OD circle analyzed. Total gravimetric loading of the filter was 0.14 mg/kg.

Scanning Electron microscope with energy dispersive x-ray spectroscopy can further reveal information about particle composition. From the HyCoRA project (Aarhaug & Kjos, 2017), information about particles collected on filters were collected.

Filter	Total	Stainless steel	Ni-P	Other metals	Oxides	Organic particles	Organic residues
HY-2	medium	+	+	+	+	+	+
HY-3	low	-	-	-	+	++	-
HY-4	medium	+	++	+	+	++	++
HY-5	low	-	-	+	+	++	-
HY-6	medium	+	++	+	-	++	++
HY-7	low	+	-	+	-	++	-
HY-8	low	-	-	-	+	+	-
HY-9	low	-	++	-	+	-	+
HY-10	low	++	+	-	+	+	-
HY-12	high	+	++	-	+	+	-



0.2 µm PTFE filter penetration

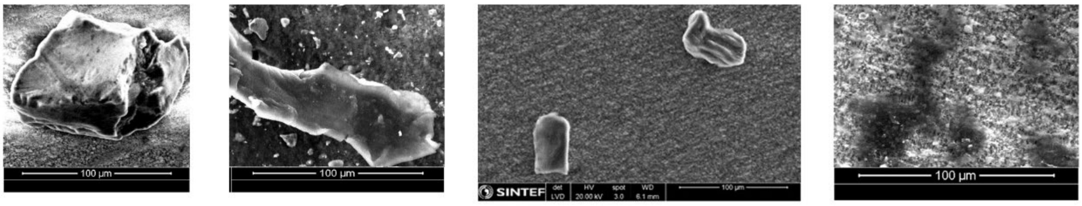


Figure 10. HyCoRA project SEM filter analysis. Table shows qualitative information about particle composition collected on samples. SEM micrograph on top right illustrates penetration of particles through 0.2 µm PTFE filter. Bottom four micrographs illustrates particles of hard, inorganic nature (left) towards soft, organic nature to the right.

Summary

This document summarizes state-of-the art for sampling of particulates from hydrogen fuel. The ASTM standardised method (ASTM D7650-21) is providing guidance for the sampling system. The ISO 19880-8 annex K is providing example of particulate sampling system. Following the new standardised method, there is several options to perform particulate samplings using different equipment, different venting system or metering system.

The table below summarise the different sampling system available and some of the important parameters of them.

Table 2. Summary of particulate sampling system available in 2020.

Sampling system	PSA-H70	HYDAC MK2	MRM-7650
Manufacturer or reference	HYDAC ASTM D7650-13 ISO 19880-1 Annex K	HYDAC ASTM D7650-21	Airborne laboratories ASTM D7650-21
Commercially available	Outdated, replaced by HYDAC MK2	yes	yes
Vent	FCEV sink	FCEV sink	Atmospheric vent system
Hydrogen metering	Recording of the HRS dispenser meter	Recording of the HRS dispenser meter	Coriolis mass flow meter with cumulative flow
Filter type available	HahneMuhle PT 020 47 BL (Ø47mm; 0.2 µm pore size)	Millipore Mitex LSWP04700 (Ø47mm; 5.0 µm pore size)	Pall TF-200 (Ø47mm; 0.2 µm pore size)

The report highlighted the fact that several parameters (presence of pressure regulator or sampling flow rate) could influence the particulate sampling and may require additional work to standardise particulate sampling best practices.

The gravimetric analysis of the filter highlighted that there are few variations in the recommended practices. The first uncertainty budget has been reported for particulate weighing with an expanded uncertainty of 85.6 µg (k=2). It is recommended to develop similar uncertainty budget for the different particulate weighing methods.

Based on the report on visual inspection of filters, a clear benefit of microscopy inspection of the filter is found beneficial and provide added information to gravimetric results.

As a perspective from this report, it has been noticed that comparison between particulate sampling strategies has not been performed. Comparison of the different sampling strategies would be beneficial to harmonise particulate sampling or demonstrate equivalence between the strategies.

References

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