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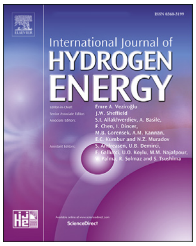

Review Article

Review of sampling and analysis of particulate matter in hydrogen fuel

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HIGHLIGHTS

- Review of known sampling methodologies for particulate matter in hydrogen fuel.
- Review of gravimetric and visual methods for assessment of particulate matter.
- Presentation of public hydrogen fuel quality data for particulates.
- Identification of challenges and shortcomings in current methods used.

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ABSTRACT

This review presents state-of-the-art for representative sampling of hydrogen from hydrogen refueling stations. Documented sampling strategies are presented as well as examples of commercially available equipment for sampling at the hydrogen refueling nozzle. Filter media used for sampling is listed and the performance of some of the filters evaluated. It was found that the filtration efficiency of 0.2 and 5 μm filters were not significantly different when exposed to 200 and 300 nm particles. Several procedures for gravimetric analysis are presented and some of the challenges are identified to be filter degradation, pinhole formation and conditioning of the filter prior to measurement. Lack of standardization of procedures was identified as a limitation for result comparison. Finally, the review summarizes results including particulate concentration in hydrogen fuel quality data published. It was found that less than 10% of the samples were in violation with the tolerance limit.

Contents

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1. Introduction

Hydrogen and its derivatives should play an important role in the decarbonization of those sectors where emissions are hard to abate and alternative solutions are either unavailable or difficult to implement, such as heavy industry, shipping, aviation and heavy-duty transport [1]. Hydrogen fuel is expanding towards large fleet and heavy-duty application for road freight, transport, maritime and aerospace as demonstrated by the expansion of infrastructure. At the end of 2021, 729 hydrogen refueling stations (HRS) were in operation worldwide [2]. The fast-paced evolution may be highlighted by the expansion of HRS in South Korea to 162 HRSs in less than 3 years [3] (ambition to reach 450 HRSs by 2025) or the recent target in Europe set by the European Commission equivalent to 3750 HRSs by 2028 (HRS every 100 km) [2].

The concentration of impurities in hydrogen fuel must be controlled for particulate and gaseous impurities. The tolerance is set to be 1 mg per kilo hydrogen by ISO 14687 [4]. Representative sampling from hydrogen refueling stations (HRS) involves collecting a sample from the nozzle as part of a normal refueling procedure.

Particulate impurities in hydrogen may source from production, storage and distribution of the fuel. For example, pyrolysis and gasification of biomass can produce tar that could produce carbonaceous particles in the gas stream [5]. In addition to introduction from said sources, particulate matter can be formed from chemical reactions and condensation of gas phase impurities. Interaction between impurities in the fuel can potentially lead to formation of condensed phase matter like acids or salts. Particulate impurities can have negative impact on the fuel cell powertrain (e.g. valves) and the fuel cell stack (e.g. catalyst surface interaction, membrane conductivity) [6].

Sampling of particulate matter in hydrogen fuel is a challenging exercise. Regulation of the dispensed flow of hydrogen fuel from the HRS without inflicting losses of particulate matter is difficult. In European project MetrohyVe (Grant number 15ENG01), it was shown that losses as high as 95% were observed when comparing regulated versus non-regulated flow for particulate sampling [7]. Birdsall [8] showed that there is a dependence on particle size and fluid flow suggesting that representative flow must be ensured when sampling of particulate material is conducted. Further, in order to ensure collection of a quantifiable amount of particulate matter on the filter, large amounts (e.g. kilograms) of accurately dispensed hydrogen fuel must be passed over the filter at relevant flow and pressure conditions.

The HRS is itself a potential source of particulate matter with potential contributions from stainless steel piping, even though it has a requirement for installation of a 5 μm size discriminating filter [9]. For fuel cell vehicles, an in-line filter of 5 or 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.

This work reviews the 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 and ISO 19880-1 Annex K. Available literature on gravimetric analysis of filters as well as visual inspection of filters is also reviewed.

2. Sampling strategies

In the following, known sampling strategies for particulate matter in hydrogen fuel are presented. Two different strategies were applied with the main difference on the HRS operating conditions (set condition by operator or following filling protocol of fuel cell electric vehicle (FCEV), e.g. SAE J2601 [10]. The first strategy is sampling the particulate from the nozzle of the HRS without FCEV as sink therefore the HRS needs to be operating in manual mode with a set flow and pressure during the overall particulate sampling. The second strategy is sampling particulate from the nozzle of the HRS when a FCEV filling is performed. In this case, the FCEV filling is operating normally with the particulate filter inserted between the nozzle and the FCEV receptacle.

2.1. Sampling system applicable for both strategies: ASTM D7650-21 standard practice for sampling of particulate matter in high pressure gaseous fuels with an in-stream filter

The standard practice [11] is applicable 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. This standard practice can be used with the two strategies (HRS in manual mode or standard filling protocol).

2.1.1. 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 2 kg. 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 [12] shall be installed. For safety, anti-whips and grounding wire shall be installed.

2.1.2. Filter housing requirements

An example of a filter housing is shown in Fig. 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.

2.1.3. Venting of hydrogen

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 [13] or UN GTR 13 [14].
2. Atmospheric vent system where the outlet should be at a minimum of 2.4 m above the ground and be placed clear of canopies that may trap hydrogen gas. A back pressure of 20 MPa should be used as to avoid high pressure release of hydrogen to atmosphere.
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.

2.1.4. Metering of the dispensed fuel

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

1. Measurement of the temperature and pressure of the tank vent system 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.

Recording of the HRS dispenser meter can only be used when using FCEV as sink.

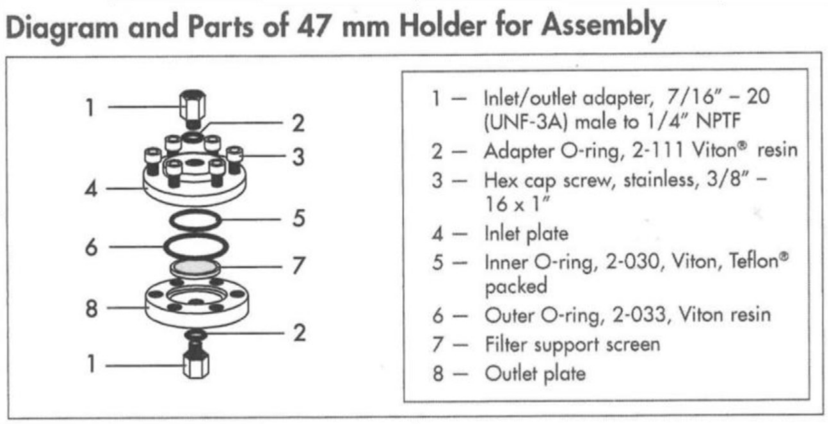


Fig. 1 – Diagram of example filter holder. Illustration by Airborne Laboratories.

2.2. *Sampling system applicable for normal filling operation: ISO 19880-1 annex K sampling procedures and hardware for hydrogen fuel quality analysis*

At the time of publication of ISO 19880-1 [9] the HYDAC PSA-H70 was not the only available commercial sampling adapter, but it was also the only sampling adapter known for 70 MPa sampling.

2.2.1. *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 of the tee, the HPSA could effectively be vented with the depressurization of the dispenser hose and nozzle. See Figs. 2 and 4 below.

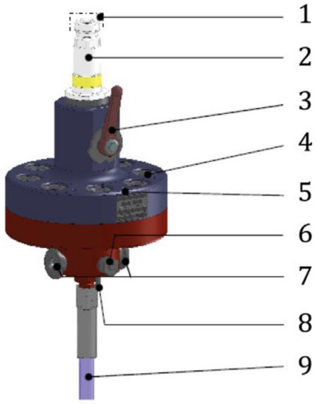
The HYDAC Operating Manual [15] lists both 0.2 μm and 5 μm filters as options to be used with the PSA-H70 adapter: Millipore PTFE Porex B 5 μm, Ø 47.0 mm or Filter membrane ALBET Lab Science PTFE hydrophob blanca 0.2 μm, Ø 47.0 mm, PT 020 47 BL. Adapter filter removal is shown in Fig. 3.

2.2.2. *HYDAC system MK2*

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 using a bleed valve. The principle is illustrated in Fig. 4.

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.

Fig. 3 – **Micron filter element removal from hydrogen particle sampling adapter unit.**



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		

Fig. 2 – **Particulate sampling adapter, HYDAC PSA-H70 shown.**

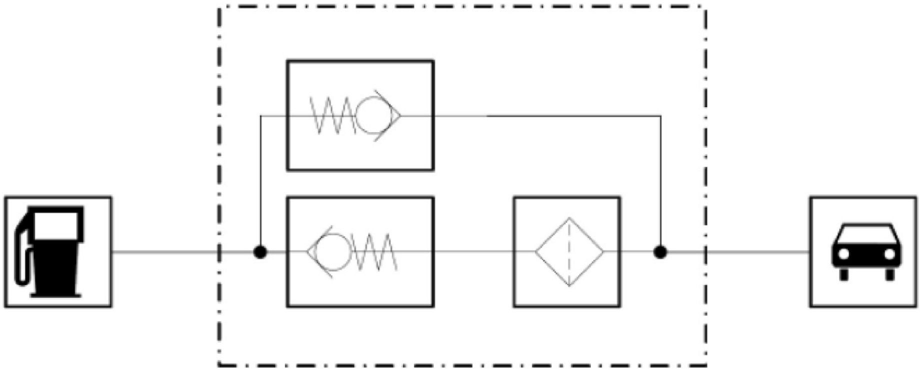


Fig. 4 – HYDAC MCP 02 PSA-H70 depressurization loop.

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 Fig. 5.

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. Neither model of the HYDAC PSA-H70 adapters have a safety relief valve as suggested by ASTM D7650.

2.3. *Sampling system applicable for HRS operation in manual mode: Airborne Laboratories MRM-7650*

Airborne Labs International offers a commercial implementation of ASTM D7650 using the MRM-7650 shown in Fig. 6. The instrument is rated at 137 MPa (20,000 psig) 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 (Strategy: HRS in manual mode). The filter housing can be replaced so that the adapter can be used for several sampling campaigns with the option of using several filter housings.

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 Fig. 7.

2.4. *Hy-Strainer T1050 heavy-duty particulate sampler*

A sampler for heavy duty (i.e., larger than 60 g/s flow) was designed by Boyd Hydrogen and NEL was made commercially available in 2022 by EV Metalværk A/S. It is a filter holder designed for heavy duty applications, e.g. flows higher than 60 g/s. It is rated for 965 bar at −40 to 50 °C that can be

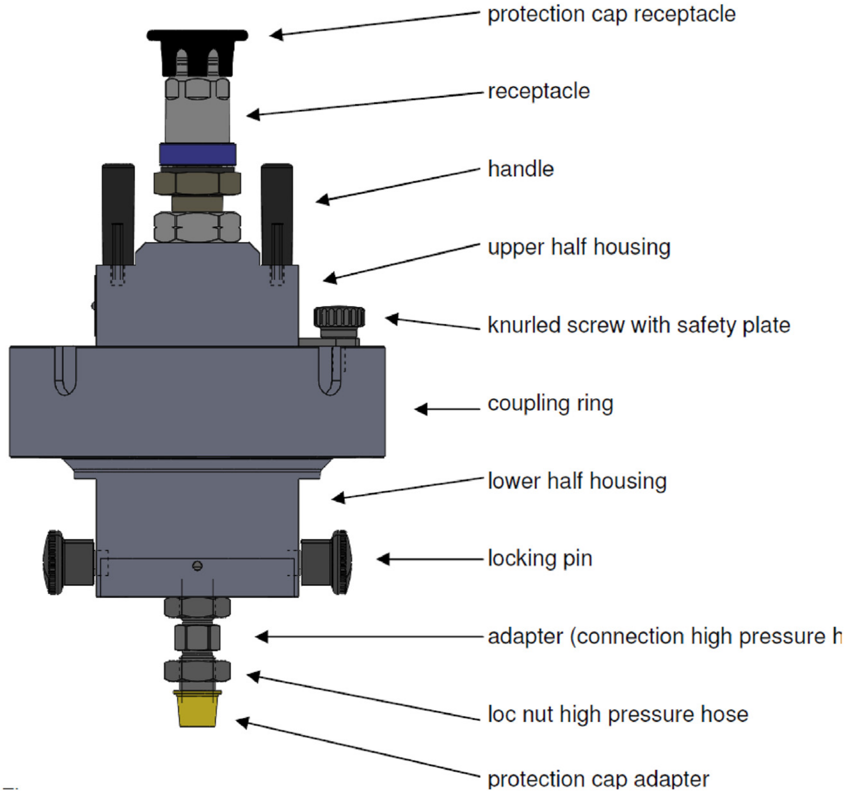


Fig. 5 – MCP 02 PSA-H70. Illustration by HYDAC.

Fig. 6 – Airborne labs MRM-7650.

incorporated into a full sampling system connecting with 1″ MP cone threads as shown in Fig. 8.

The sampling adapters are compared side-by-side in Table 1.

3. Discussion

3.1. *Selection of filters for particulate sampling*

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

In ASTM D7650-13 [16], use of a 0.2 μm PTFE filter of diameter 47 mm was referenced: Pall TF-200 47 mm 0.2 μm (P/N 66143). The filter has two sides, polytetrafluoroethylene (PTFE) and propylene. Only the PTFE side faces incoming hydrogen fuel and collects particulates in hydrogen.

Other filters referenced are summarized in Table 2.

Several filter types (pure quartz, fibrous, and porous PTFE filters) were evaluated for hydrogen application in MetroHyVe Deliverable 3 report [17]. 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 a few bar overpressure.

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.

3.2. *Filtration efficiency*

In order to compare filtration efficiency for 5 μm and 0.2 μm filters, a laboratory setup with generation of 300 nm polystyrene latex spheres (PLS) were used to test filters [18] shown in.Fig. 9.

It was found that the filtration efficiency for 5 μm and 0.2 μm filters were on average 99.80% and 99.94%. At the 95% confidence level, the mean values were not found to be significantly different. The result is shown in Fig. 10.

Further, filtration efficiency was evaluated for 200 nm PLS particles. No significant difference was observed. For previously exposed filters of type 0.2 μm, it was found that filtration efficiency was significantly lower for filters already exposed to particulate matter: 99.90% vs. 94.66%. Therefore, filters should not be re-used after being exposed to hydrogen.

3.3. *Gravimetric analysis of filters*

There are several challenges associated with analysis. Amongst these are:

- Filter degradation from exposure to hydrogen
- Pinhole formation
- Filter curling
- Proper conditioning of filter (T, RH)

Filter degradation has been observed for quartz fiber filters due to swelling of the fibers [17]. In addition to potential mass

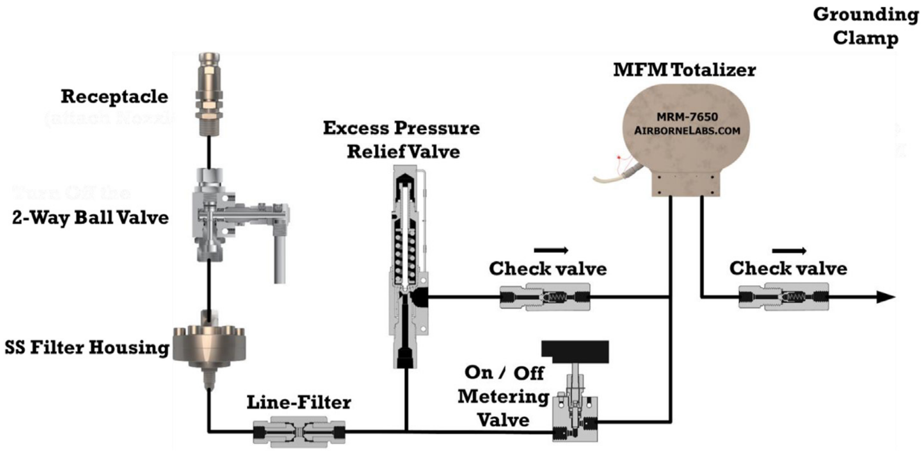


Fig. 7 – Schematic of the MRM-7650.

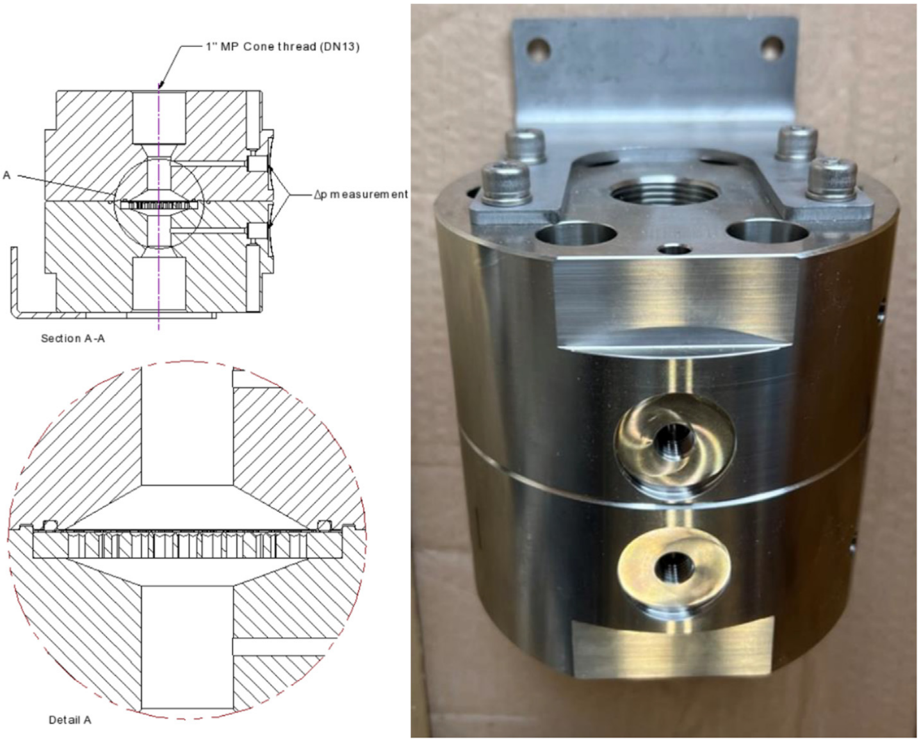


Fig. 8 – Hy-Strainer T1050 schematic and picture.

Table 1 – Summary of particulate sampling system available in 2023.

Use/Application	Light-Duty sampler	Light-Duty sampler	Light-Duty sampler	Heavy-Duty sampler
Sampling system	PSA-H70	HYDAC MK2	MRM-7650	Hy-Strainer T1050
Manufacturer or reference	HYDAC ASTM D7650-13 ISO 19880-1 Annex K	HYDAC ASTM D760-21 ISO 19880-1 Annex K	Airborne laboratories ASTM D7650-21	EV Metalværk A/S for Boyd Hydrogen/NEL
Commercially available	Outdated, replaced by HYDAC MK2	yes	yes	yes
Vent	FCEV sink	FCEV sink	Atmospheric vent system	Vent to atmosphere/ vehicle/simulated tank
Hydrogen metering	Recording of the HRS dispenser meter	Recording of the HRS dispenser meter	Coriolis mass flow meter with cumulative flow	Recording of the HRS dispenser meter
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)	Ø47mm test chamber

losses, curling of the filters makes gravimetric analysis challenging. Pinhole formation in the filters have occasionally been observed [19]. In addition to loss of particulate matter, the pinhole formation can potentially constitute a loss of filter mass. The pinhole formation is expected to be a function of particle momentum, but since hydrogen flow velocity is normally not registered data for sampling little is known about the impact. It has been speculated that pre-cooling of hydrogen to −40 °C could potentially freeze water at close to tolerance levels (i.e. 5 ppm). Ice could thus form pinholes in the filter.

On several occasions, negative masses of particulates have been registered for particulate sampling from hydrogen fuel [19]. During the project MetroHyVe 2 (Grant agreement 19ENG04), repeated particulate sampling were performed in short time at a hydrogen refueling station varying FCEVs and refilling time. The results obtained on three out of five measurements presented negative particulate mass (values ranging from −0.65 mg/kg to 0.67 mg/kg). Uncertainty estimates for the gravimetric analysis reveal that the negative masses registered are much larger than the uncertainty. NPL investigated the impact of relative humidity (RH) on the gravimetric results. For quartz fiber filters, worst case, the impact was 2.8 μg/% RH [17]. An error of about 14 μg would fall in the 5% allowable range in RH conditioning. This is much smaller than the negative masses observed. Several operations parameters may contribute to this phenomenon: pressure impact on the filter (i.e. visible mark on filter after sampling), mass of hydrogen sampled, transportation, delay and condition of analysis.

Table 2 – Filter parameters used for particulate sampling.

Filter reference	Filter type	Pore size	Thickness	Equipment or method use	Comment
Pall TF-200 47 mm	PTFE Membrane Disc Filters	0.2 μm	139 μm	ASTM D7650-13 MRM-7650	Filter has two sides
Millipore Mitex Ref LSWP04700	hydrophobic PTFE	5.0 μm	170 μm	HYDAC PSA70 MK2	Unable to be used in particulate filter autohandler
Millipore PTFE Porex B	PTFE	5.0 μm	n.a.	HYDAC PSA70	Not commercially available in 2020
HahneMuhle Ref PT 020 47 BL	PTFE reinforced by a Polypropylene net	0.2 μm	160 μm	HYDAC PSA70	
HahneMuhle Ref PT 500 47 BL	PTFE reinforced by a Polypropylene net	5.0 μm	180 μm	HYDAC PSA70 MK2	
Omnipore Ref JGWP04700	Hydrophobic PTFE polymer membrane bonded to a high-density polyethylene support	0.2 μm	65 μm	ASTM D7650-13	

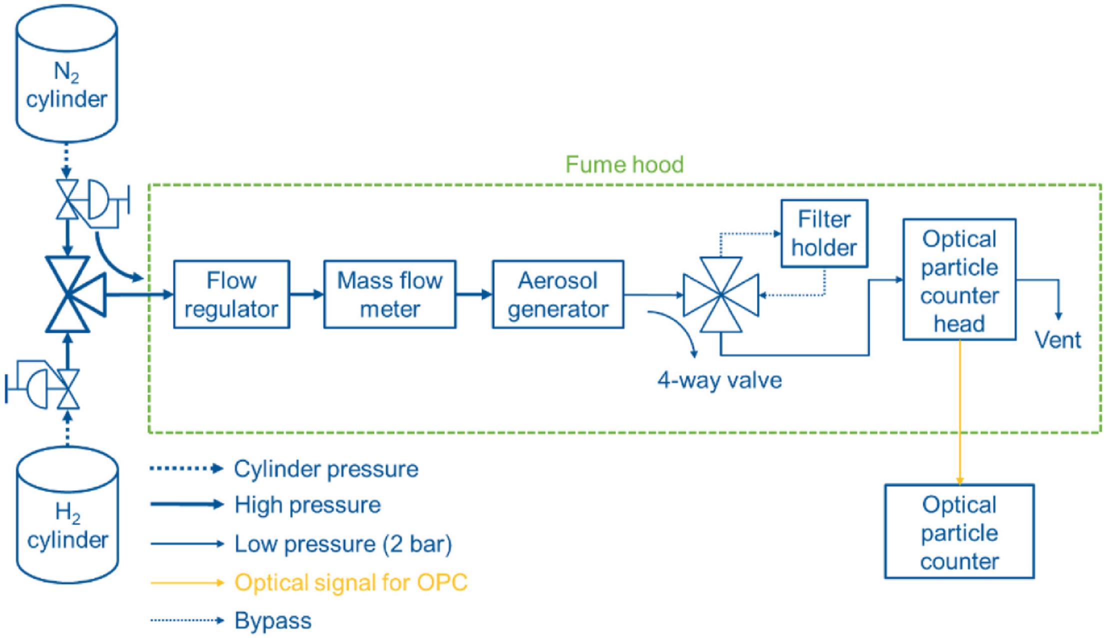


Fig. 9 – Experimental setup for the determination of filter filtration efficiency. The experiment was conducted at low pressure (2 bar).

3.3.1. *Description of gravimetric analysis methodologies*

The different methodologies for the gravimetric analysis are given in the following section. As, the procedures do not converge, they are sequentially listed.

3.3.1.1. *ASTM D7651-17 standard test method for gravimetric measurement of particulate concentration of hydrogen fuel.* ASTM D7651-17 [20] is a protocol for conducting gravimetric analysis of filters. Important details from the protocol are given in the following.

3.3.1.1.1. *Filter handling*. Filter should be at all times handled with powder-free gloves. Filter equilibration for at least 24 h in controlled (i.e., temperature and moisture) environment is prescribed. US EPA conditions for PM10 samples are given as example: 19–23 °C and 30–40% RH.

3.3.1.1.2. *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.

3.3.1.1.3. *Glove box*. A glove box is typically used to provide a controlled atmosphere for the balance. A clean atmosphere with 30–40% RH is typically provided with nitrogen gas. A static charge removal device is required to prevent charging and potential loss and agglomeration of particulate matter.

3.3.1.1.4. *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.

3.3.1.1.5. *Method precision and bias*. Whereas terminology is defined in the method, performance data is not given.

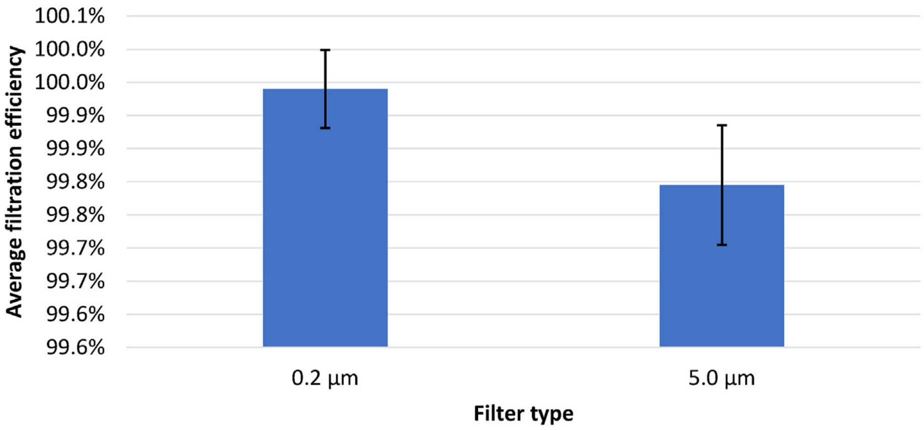


Fig. 10 – Filtration efficiency of 5 μm (99.80%) and 0.2 μm (99.94%) filters with 300 nm PLS particles. Error bars is for 95% confidence (k = 2).

3.3.1.1.6. *Cleaning of the sampling adapter*. Under a HEPA filter horizontal flow hood, the filter holder components are cleaned by immersion in 1000 mL beaker filled with de-ionized water. Sonication using either sonic probe or ultrasonic bath is performed for at least 20 min. Water is decanted and the procedure is repeated two more times. The filter holder components are then dried in a mini clean room for two days at 15–30% relative humidity.

3.3.1.2. *HYDAC MCP 02 PSA-H70 operations manual*. The operations manual for the MCP 02 PSA-H70 sampling adapter has a section dedicated to laboratory analysis of the filters used to collect particulates [21]. The manual gives general reference to ASTM D7651-10 [22], however the manual differs from this protocol on several occasions.

3.3.1.2.1. *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 [23].

3.3.1.2.2. *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 [24]. This implies that the clean room atmosphere must contain no more than 352 000 particles >0.5 μm per cubic meter and 60 HEPA filtered atmosphere changes per hour.

3.3.1.2.3. *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 [23].

3.3.1.2.4. *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.

3.3.1.2.5. *Gravimetric analysis*. Conditioning of the filter and filter support are to be conducted in a drying oven at 85 °C for approximately 45 min before cooling for an additional 30 min in a desiccator.

3.3.1.2.6. *Balance*. A requirement of a resolution of 300 μg is stated.

3.3.1.2.7. *Cleaning of the sampling adapter*. The sampling adapter is cleaned with a high purity solvent. Heptane (p.a. 99.99%) is mentioned as one 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.

3.3.1.3. *MetroHyVe good practice guide for the handling, transporting and weighing of filters from particulate sampling in gaseous hydrogen*. This Good Practice Guide [17] aspires to document a 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.

3.3.1.3.1. *Method*. The method is applicable to collection of masses between 25 μg and 8 mg, with a maximum mass of filter and collected particulates no higher than 300 mg.

3.3.1.3.2. *Sample storage*. In order to avoid evaporation, the 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.

3.3.1.3.3. *Balance*. A balance with a resolution of 0.1 μg was specified. For PTFE filters a faraday cage pan is prescribed. A detection limit of 5 μg/kg is recommended [4].

3.3.1.3.4. *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.

3.3.1.3.5. *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.

3.3.1.3.6. *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 [25], there is a limit for 40 μg and 60 μg in mass difference within a 24-h period for sampled and unsampled filters respectively.

3.3.1.3.7. *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.

3.3.2. *Challenges with gravimetric analysis*

The different methodologies clearly show differences. There is a need to support standardization of the different methodologies, for example definition of the balance requirement. The different balance recommendations range from resolution of 0.1 μg–300 μg. The conditioning method seems to vary with various conditions recommended (temperature, oven, time). It would be beneficial to compare methodology and standardize best practice to ensure better repeatability.

The choice of filter type is not well documented. The coexistence of two different pore size may create discrepancies in the results provided. The MetroHyVe 2 study observed significant variation of repeatability between filter pore size (0.2 μm pore size versus 5.0 μm pore size) during repetitive sampling (same day, same HRS). Additional studies are needed to support understanding on the parameters impacting the repeatability of the measurement and support standardization of the filter pore size.

From a metrology point of view, it has been suggested that there is a lack of traceability for particulate measurements [26]. Method validation development and better understanding of the uncertainties is required in order to ensure the measurement is fit-for-purpose. Further, it was suggested that strategies for online particle analysis could be explored with e.g. a Tapered Element Oscillating Microbalance as an alternative to sampling and subsequent analysis.

3.4. *Visual inspection*

Earlier standards for hydrogen fuel quality (e.g., SAE J2719 [27]) had a requirement of particulate size being smaller than 10 μm in addition to the concentration requirement of 1 mg/kg. It was thus common practise to perform visual assessment of the filters in order to estimate particle size.

As part of the H2 Moves Scandinavia demonstration project, fuel quality was monitored for HRSs in the Oslo area [28]. Optical microscope was used to assess the particle size according to ASTM D7634 [29], as shown in Fig. 11.

Scanning electron microscope (SEM) with energy dispersive x-ray spectroscopy can further reveal information about particle composition. From the HyCoRA project [19] information about particles collected on filters were collected as shown in Fig. 12.

4. Published data on hydrogen fuel quality

Limited data is published on dispensed hydrogen fuel quality and often excludes particulates [30,31]. The NREL database [32] reports that 1 out of 9 the samples analysed for particulate matter in the period 2015Q4 to 2022Q2 is not within SAE J2719 [27] specification. For particulate matter, only 9 out of 700 samples collected in the period 2015Q4 and 2022Q2 were analyzed. One sample was found to be out of spec with >1 mg/kg H_2 and one sample was found to be in the range 0.8–1.0 mg/kg H_2, the rest being in the range of 0–0.2 mg/kg H_2 except for one sample where particulate matter was not detected.

As part of the H2Moves Scandinavia demonstration project, three HRS in Oslo were checked for H_2 quality [28]. The concentration of particulates found in the three HRS checked was found to be 0.042, 0.14, and 0.21 mg/kg H_2.

As part of the 2nd sampling campaign performed in the HyCoRA project, particulate concentration in eight out of ten samples was assessed [19]. For all samples, the concentration was well below the tolerance limit. The 95% single sided confidence level was calculated from the combined uncertainty of the gravimetric analysis of the filter and the uncertainty in mass of hydrogen dispensed. Generally, the uncertainty of the gravimetric analysis is high and for one sample this resulted in a confidence interval outside the tolerance limit. The results are illustrated in Fig. 13.

For HyCoRA 3rd sampling campaign, only negative particulate mass was reported [19]. The uncertainty in gravimetric

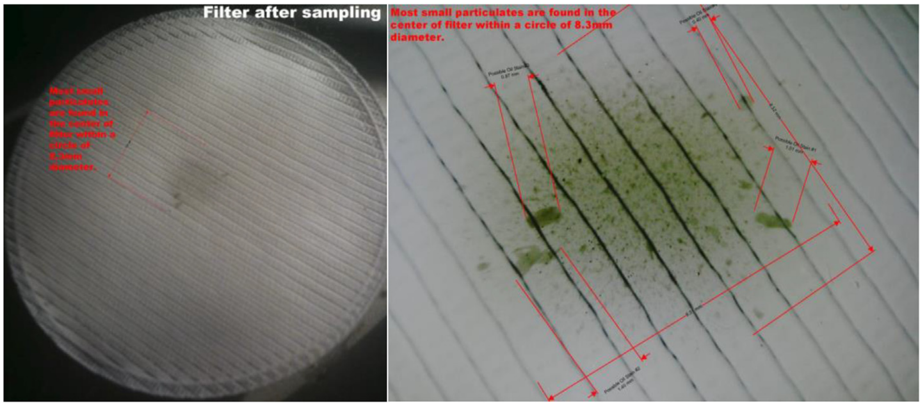
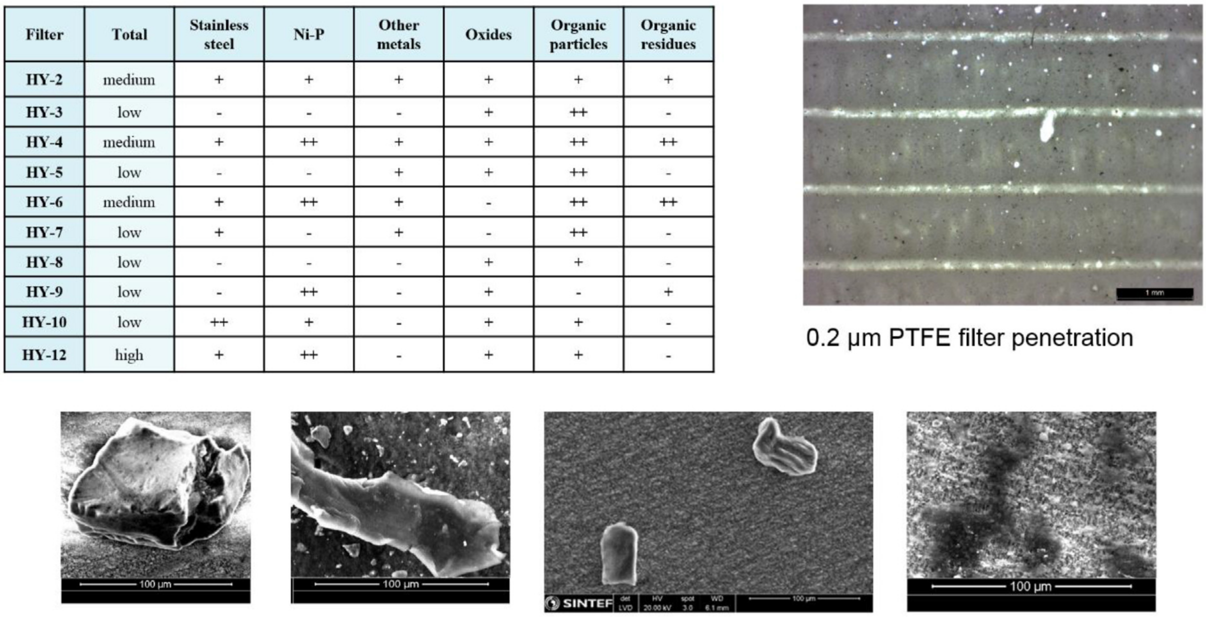


Fig. 11 – Optical microscope inspection of filter. Picture to the right is magnified 27 times and identifies green, oily residue. Four large spots of diameters 1.4, 1.0, 0.87 and 0.40 mm. 48 particulates of diameter larger than 0.02 mm were found in the 8.3 mm OD circle analysed. Total gravimetric loading of the filter was 0.14 mg/kg. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



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	+	++	-	+	+	-

Fig. 12 – 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.

analysis was reduced by better control of filter conditioning. Nevertheless, the mass after sampling was lower than before sampling for all filters. It highlights a potential bias from the sampling methodology (mass loss) in real life conditions.

Smart chemistry has conducted a comprehensive study of particulate matter in hydrogen dispensed from HRS in the US [33]. Using ASTM strategies for sampling [16] and analysis [20], they found from a set of 81 samples that 94% contained particulate matter. The highest concentration recorded, 0.24 mg/kg, was not in violation with the prevailing standard for hydrogen fuel [4]. Monitoring of newly commissioned HRS and HRS with stainless steel tubing replacement revealed a peak with subsequent decay of particulate matter content suggesting tubing to be a source. An investigation of inline 10 μm filters were also performed. Filters installed upstream and downstream HRS dispensing regulation were compared with an unused filter with respect to particle contamination analysed in water after sonification. Interestingly, except for Mn, Ni, Zn and Si, several metals (Fe, Cr, Ca, Cu) were found to be most abundant in the unused filter. Filter upstream HRS regulator was found to be more contaminated than the downstream installation, but both are cleaned by the flow of hydrogen. The study concluded that new filters need cleaning before installation. Evidence of polymeric coatings was also discovered in several filter samples, suggesting degradation of materials used for surface protection.

As part of the Hydraite project, a survey was conducted to identify new impurities in hydrogen fuel [34]. The result indicates several potential sources of particulate and condensed matter. This is listed in Table 3. Potential poisoning components identified in Hydraite project survey.

In addition to the particulates, many of the other poisonous components identified could appear in condensed form and thus be trapped on the sampling filter.

For maintenance, piping was identified the main source of poisonous components. Here, particulates were listed in addition to other possible condensing species like oil, sulfurs and detergent (sodium salt, acetone, alcohol, sodium hydroxide and sodium salts).

It is emphasized that these results are based on survey feedback from stakeholders and not a result of published scientific work on the topic of sampling and analysis of hydrogen.

5. Conclusions

This review summarizes state-of-the art for sampling of particulates from hydrogen fuel. ASTM D7650-21 [11] is providing guidance for sampling of particulate matter. ISO 19880-1 provides an example of commercial sampling device [9]. Gravimetric analysis of filters is described in ASTM D7651-17 [20]. Under development is the standard ISO 19880-9 [35] which will cover all aspects of sampling of particulate matter.

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 standardize 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 review, it has been noticed that comparison between particulate sampling strategies has not

Fig. 13 – Particulate content in hydrogen samples collected at the nozzle with HYDAC PSA-H70 sampling adapter.

Table 3 – Potential poisoning components from built in HRS components identified in Hydraite project survey [34].

Component	Pot. poisonous component	Possible damaging effect
Sealing gasket	Si (Silicon)	PFSA membrane contamination
Sealing gasket	Tetrachloro hexafluoro butane	
Compressor	Oil component	Water management problem, transport properties electrolyte membrane
New SS tubing	Particulates	Abrasion
Valves	Particulates	Abrasion
Seals	Particulates	Abrasion
Filter	Particulates	Abrasion
Polymeric coating	Delaminated coating components (Me, Carbon, Cl, P, Silicon, S)	Abrasion, transport properties electrolyte membrane, performance drop, catalyst
Sealing	Sulphur vulcanized FKM, EPDM with carbon black as filler	Abrasion, poisoning catalyst

been performed. The study highlighted the need for standardising some aspect as the gravimetric analysis, the filter pore size, and a comparison of the sampling strategy. Furthermore, a comparison of the different sampling strategies would be beneficial to harmonise particulate sampling or demonstrate equivalence between the strategies.

Considering the exponential increase in HRSs worldwide, it is becoming urgent to harmonise or provide new guidelines for particulate sampling at HRS. Otherwise the industry may face discrepancies in results providing by various methodologies and operators as highlighted in this review. This could lead to undetected issues to the FCEVs in operation.

5.1. *Future requirements for sampling*

Heavy duty hydrogen fueling is under development, both when it comes to establishment of fueling protocols as well as nozzle geometries. Both medium and high flow geometries have been proposed so that flows up to 300 g/s is under consideration. ISO TC 197 WG24 aims to standardize heavy duty refueling.

For sampling of particulates, a fundamental understanding of the impact of pressure and flow is important so that protocols for representative sampling can be established. Filter integrity is another topic that needs to be investigated when higher flows are applied to the sampling adapter. The project MetHyTrucks (Grant agreement 22NRM03) funded by EURAMET was started in 2023 to address some of these knowledge gaps.

Declaration of competing interest

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

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