METROLOGY for HYDROGEN VEHICLES

REPORT:

Feasability study for developing a method to utilize a Tapered Element Oscillating Microbalance (TEOM) for measuring particulate concentrations in hydrogen gas

EMPIR EURAMET

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This guide was written by:

Jordan Tompkins	NPL	jordan.tompkins@npl.co.uk
Paul Buckley	NPL	paul.buckley@npl.co.uk
David Butterfield	NPL	david.butterfield@npl.co.uk

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1 - Introduction

1.1 Task objectives under MetroHyVe

The aim of this task is to investigate the feasibility of using a Tapered Element Oscillating Microbalance (TEOM) model 1405 (Thermo-Fischer) to provide real-time measurements of particle mass in hydrogen gas samples at Hydrogen Refueling Station (HRS) facilities [1]. This report details the initial testing of the TEOM instrument using hydrogen gas that has been doped with particles, the results of the testing, the potential shortcomings and the scope for additional work that needs to be carried out before this instrument can be used in a commercial setting.

1.2 Scope of the Feasibility Study

Particulate contamination is found in hydrogen and 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 real-time would represent a significant upgrade on the timeframe of the current measurement system, which involves collecting particle contaminants on a pre-weighed filter and reweighing after sampling. This study is intended to provide an initial framework for how to safely conduct measurements using a TEOM instrument and hydrogen gas.

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 m^{-3} set for particles [1]. 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 [6].

Particles in the hydrogen gas can originate for a number of different sources, potentially related to the initial fuel source, production methods and storage methods [2], [3], [4], [5].

Contamination of the initial fuel source used during the production of hydrogen gas with compounds such as water, ammonia, sulfur compounds or formic acid [2]. These compounds can lead to the formation of acids or salts within the gas stream or on the surfaces of storage units or fuel cell components [3], [4], [5]. 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 [3]. 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 [5].

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

These considerations originate from NPL's process in devising and constructing the sampling system incorporating the TEOM instrument and high-pressure atomiser (HPA) for the generation of particles in the gas stream. 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 TEOM and hydrogen gas for the first time.

- The standard operating conditions of the TEOM instrument are a 3.0 l min^{-1} sample flow and 13.67 l min^{-1} bypass flow. In order to minimize the risk related to working with hydrogen, the sample flow rate from the hydrogen cylinder was reduced to 1.0 l min^{-1} and the bypass flow was reduced to 10.0 l min^{-1} and was drawn directly from a nitrogen cylinder. The levels of hydrogen present in the system should fall outside of the explosive range, 4 – 77%

- A 3 m tall exhaust line was attached to the outlet of the pump, featuring a flame damper and diffuser at the outlet. This should prevent any potential build-up of hydrogen gas at the outlet and prevent any ignition of the hydrogen gas in the sampling system

- In an effort to prevent interferences from volatile and semi-volatile species, the TEOM column and oven are heated to 50 °C, a temperature below the auto-ignition temperature of hydrogen gas

- The system was designed using exclusively stainless-steel tubing and stainless-steel Swagelok® fixtures, with the exception of the tubing at the rear of the TEOM, and the exhaust line, which were nylon. The nylon tubing was the standard tubing that came with the TEOM as was shown to not leach hydrogen. Therefore, it was shown that it was not necessary to replace this tubing as it was all downstream of the TEOM and particle losses were not a concern. The inlet of the TEOM was adapted so it could be directly attached to the HPA. This involved removing the standard PM head, and flow splitter, and attaching an adapted stainless-steel fixture to the inlet line

- In the HPA, a solution of deionised water and polystyrene latex (PSL) beads, with a nominal size of 900 nm (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 Tapered Element Oscillating Microbalance (TEOM)

The TEOM instrument used in this experiment was a Thermo-Scientific® model 1405 [1]. This is a 'gravimetric' instrument that draws, then heats, ambient air or gas samples through a filter at a consistent flow rate, continuously weighing the filter and calculating the mass concentrations of any PM present. The instrument should be calibrated on a regular basis, adhering to the manufacturer's specifications. A built-in leak check program should also be run prior to testing to ensure the system is sealed.

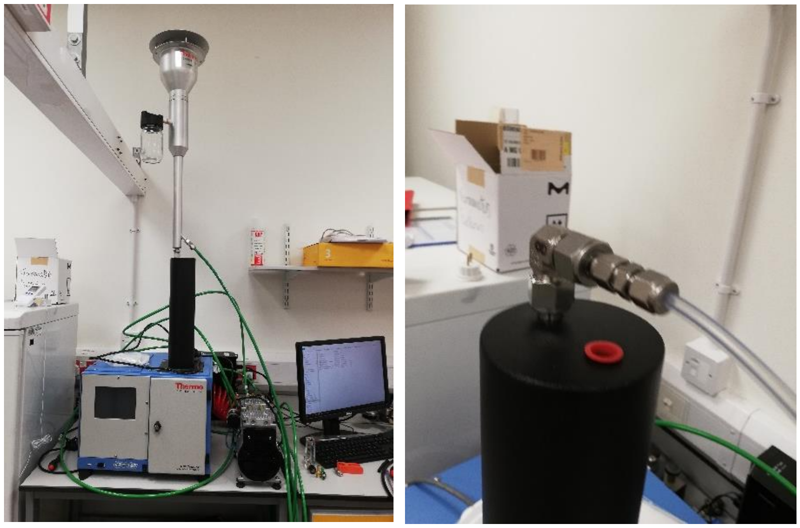

Figure 1: TEOM instrument used for particulate sampling at NPL and adapted inlet system

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.

Figure 2: TOPAS® atomizer ATM 210 system

2.3 Sampling system design and procedure

The testing system was setup as shown in Figure 3. Prior to testing, the TEOM system was leak checked and new a new filter was mounted in the sample line of the TEOM prior to testing taking place. In addition, once the system was constructed, a hydrogen leak detector (from IPS Hydrogen Power) was used to ensure no significant leaks were present during the experiment. No significant leaks were detected from the TEOM system shown below during the experiment. However, a small leak was found originating from the HPA, which was sealed after appropriate re-tightening of connections. No hydrogen leaks were detected at the rear of the TEOM instrument where the stock nylon tubing was used for the bypass flow and exhaust connection to the pump.

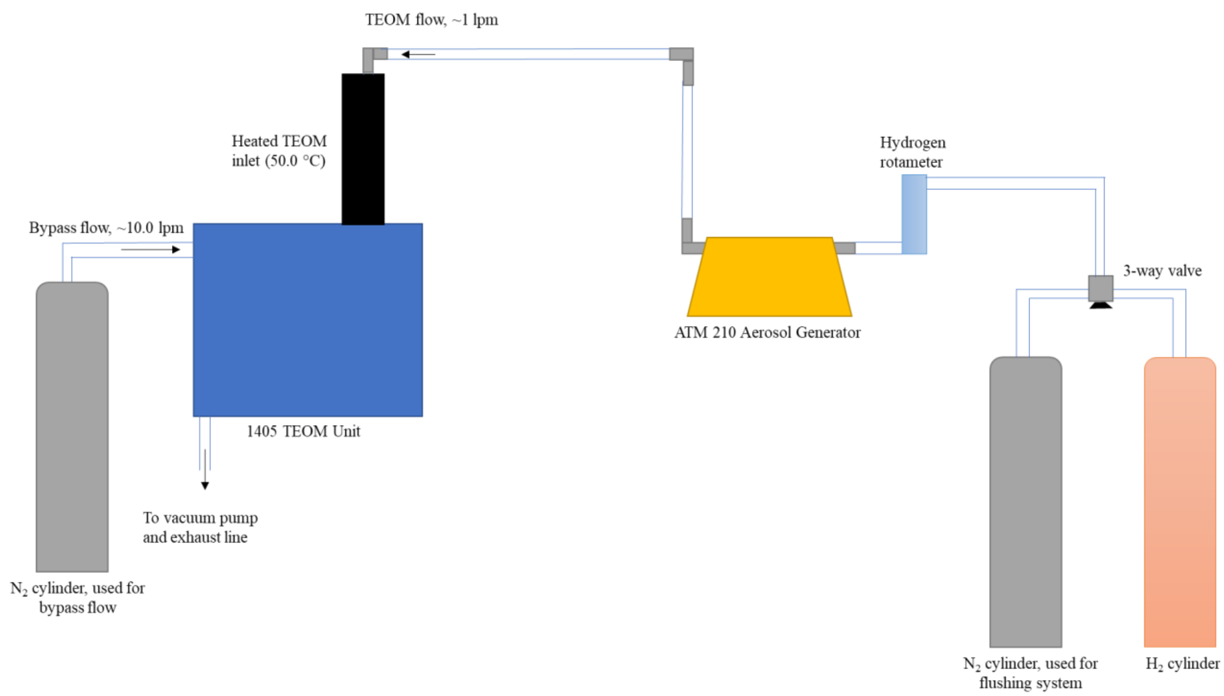

Figure 3: System design for feasibility test, indicating flow directions and flow rates

Figure 4: High Pressure Atomizer, H_2 Rotameter and TEOM instrument used during testing

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

1. The TEOM system 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

2. The sampling system was constructed using the stainless-steel tubing and fittings described above

3. The relevant regulators were attached to all cylinders and tested for pressure retention

4. The 900 nm PSLs and deionized water solution was added to the HPA and the system was resealed

5. The system was then leak checked using the internal "Leak Check Wizard" installed in the TEOM instrument

6. Once a satisfactory result was obtained after the leak check, the bypass flow line was connected to the N_2 cylinder designated as the bypass flow cylinder. The three-way valve

system was then connected to the N_2 cylinder and H_2 cylinder designated for the sampling and system flushing, ensuring the switch was positioned to draw from the N_2 cylinder

7. The bypass flow N_2 cylinder and system flushing N_2 cylinder were both opened to ensure gas was flowing through the system and all air was evacuated from the sampling system

8. The hydrogen rotameter was opened to ensure the required sample flow was moving through the system and the flow rates were checked on the instrument interface

9. The system was left for approximately 30 minutes to allow sufficient time to equilibrate

10. Once a response was registered on the TEOM instrument interface, the three-way valve was switched to sample from the H_2 cylinder. The hydrogen rotameter was checked to ensure the flow was properly regulated and the handheld leak check device was used to ensure that there were no significant leaks in the testing system

NOTE: Should any leaks be detected, the area should be cleared, and, if possible, the H_2 cylinder should be closed to remove the source of the fuel gas. Upon making the system safe, it should be flushed with N_2 before resuming work.

11. The system should again be left to sample for a period of approximately 10 – 15 minutes, to allow enough time for mass to be collected

12. Once the sampling period is concluded, the three-way valve should be switched back to the N_2 cylinder to flush the system again prior to further testing or shutdown.

2.4 Calculations and Sampling Results

The mass of the particles collected on the filter are calculated based on the oscillations of the microbalance in the sample line, based on the following equations;

$$f = (K/M)^{0.5}$$

where:

f	= frequency
K	= spring constant
M	= mass

K and M are in consistent units. This relationship between mass and change in frequency can be expressed as:

$$dm = K_0 \frac{1}{f_1^2} - \frac{1}{f_0^2}$$

where:

dm	= change in mass
K_0	= spring constant (including mass conversions)
f_0	= initial frequency (Hz)
f_1	= final frequency (Hz)

These calculations are performed internally in the instrument and the final mass (M) is calculated and can be downloaded by the user. This download can be carried out using a USB stick or via an RS-232 connection with an accompanying laptop or PC. In the interest of limiting the electronics present at the testing location, it was decided to download the data onto a USB stick once testing was completed.

The results of the measurement period are shown in Figure 5. After the initial stabilization period, the TEOM registered a mass recording while nitrogen gas was used as the carrier gas. Upon switching to hydrogen as the carrier gas, a large negative value was recorded. This is potentially due to the filter dynamics being disrupted by the change of carrier gas from nitrogen to hydrogen. A significant peak in mass concentration, approximately 2400 µg m^{-3}, was observed after the system was flushed with nitrogen and the gas stream was cut off and the system returned to ambient sampling. This indicates that a large amount of particulate matter was deposited on the filter during the experiment. The subsequent decrease in mass after the peak is indicative of a loss of mass associated with the evaporation of water deposited on the filter.

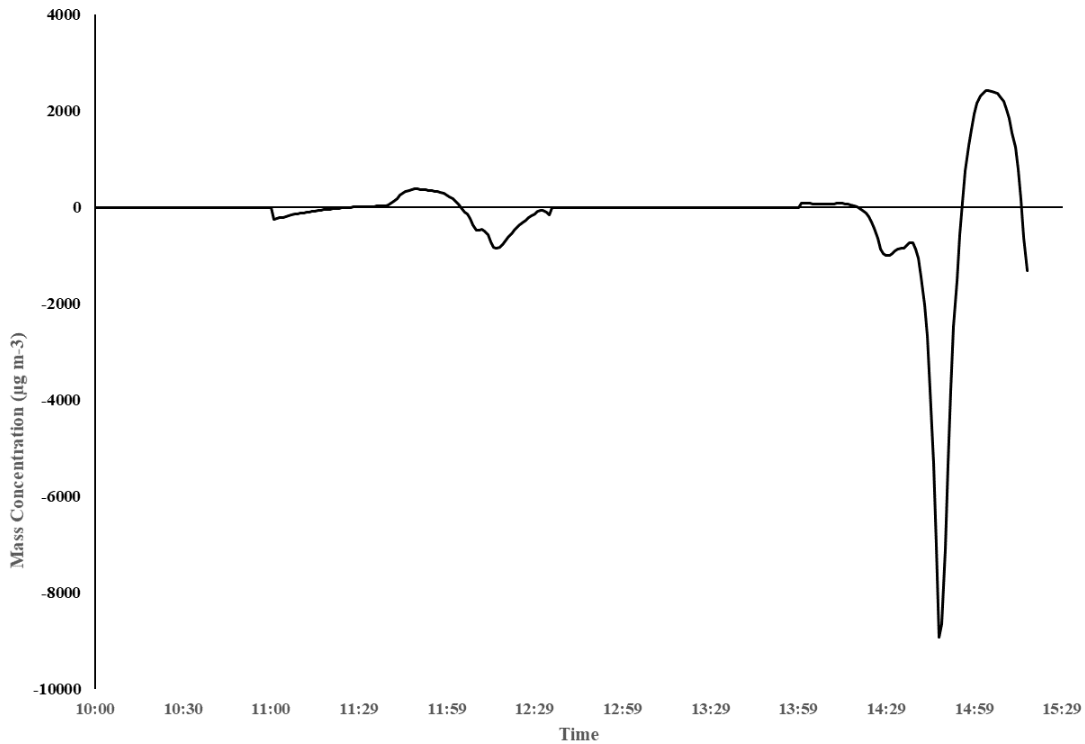

Figure 5: Results from testing of the TEOM sampling system with Nitrogen and Hydrogen

3 – Conclusions

This Feasibility Study is intended to be used as a helpful document for those wishing to set up their own measurement system for the determination of the mass of particulates in hydrogen. In line with the objectives set out in the MetroHyVe EMPIR project, this study has highlighted the initial considerations for using a TEOM instrument for in-line sampling of particulate contaminants in a hydrogen gas stream. It has been demonstrated that the instrument works in principle, and the risk assessment successfully mitigated any potential sources of danger.

It should be noted that further testing of the system should be carried out using a different particle generator as the potential interference from water droplets was identified during this feasibility study. The only leaks identified during the experiment also originated from the atomiser system. The potential for interference from the changes in carrier gas has also been identified here.

If the experiment were to be repeated, a longer time period of minimum an hour, should be allowed for system stabilization following the change of carrier gas. The oscillating frequency of the instrument should also be recorded as well as the calculated mass measurements. This would allow the user to calculate the mass concentrations independently of the instrument, allowing the user to verify the results from the instrument and potentially adjust the calculations based on the properties of the carrier gas.

The experiments carried out in this study have demonstrated that the TEOM instrument can safely operate using hydrogen gas. Due to the restrictions in place relating to the current COVID-19 crisis, it was not possible to test this system for an extended time period, or at the HRS as initially proposed in the project outline. Continuation of this project should focus on rectifying the issues identified in this report and testing the system in a commercial setting.

4 – References

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