METROLOGY for
HYDROGEN VEHICLES

REPORT:

A4.3.8: Sampling using sorbent tubes directly at the HRS – assessment of the feasibility

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This report was written as part of activity A4.3.8 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.

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1 - Introduction

Among the characteristics for the fuel specification that are listed in Table 1 of the standard ISO14687-2, three are total species: Total hydrocarbons (Methane basis), Total sulphur compound (H2S basis) and halogenated compounds (Halogenate ion basis). Determination of total species is a real analytical challenge from a metrological point of view. A total compounds family cover a large number of species with physical properties (molecular weight, polarity, boiling point…) which vary greatly within the family.

As many of the compounds belonging to the “total” species are organic, using sorbent tubes can allow detecting many compounds of one or more families in one analysis. ; using the right sorbent and the adequate sampling volume, organic impurities belonging to hydrocarbons, halogenated compounds and sulfur compounds will be trapped and retained on the sorbent while the hydrogen will pass through. This will lead to an enrichment of the targeted compounds enabling challenging detection limits to be reached. However, for very volatile compounds such as HCl, H_2S, CH_4, the method is not recommended.

The efficiency of sorbent tubes has been assessed in activities A4.3.4 (for total halogenated compounds), A4.3.5 (for sulphur compounds) and A4.3.6 (for total hydrocarbons).

Even through the results show that not all compounds belonging to the three total species to be analysed when performing hydrogen purity analysis can be quantified on one unique sorbent, the study clearly shows that the method is promising for total species. A multibed sorbent consisting of Tenax TA (weak), Carboxen 1003 (medium), Carbograph 1 (strong) is shown to be a versatile sorbent suitable for the three “total species”; only a few compounds from each family would need to be analysed using other analytical methods. This method proposed here for total species will not only provide a sum of concentrations but also an identification of which compound(s) is/are actually present in the hydrogen.

In this report, we have assessed the feasibility of sampling on sorbent tubes directly at the station.

2 - General considerations about sorbents

2.1 – Inlet Pressure

Very few documents discuss the maximum pressure that can be applied at the inlet of the sorbent tube.

According to Markes International [1], specialist of analytical desorption instrumentation, there is no clear limit for the pressure in the inlet of sorbent tubes. However, if high pressure source is connected directly to the sorbent tube, this quick release would result in a very high flow rate. This high flow through the tube could severely damage the tube by pushing the sorbent out. Therefore Markes would recommend having a 2-stage regulator in-line to step down the pressure.

However when reducing the pressure, risk for adsorption in the regulator must carefully be assessed and it may require using treated regulators.

Markes is currently performing a study where sorbents are tested at pressures up to 8 bar. Even higher pressures are now tested. However, it is impossible to work with tubes at the pressure delivered at the station, 700 bar.

In any cases, some precautions need to be taken: the tube should for example have retainer on both sides of the sorbent (but it should be insured that compounds do not adsorb on the retainer at the inlet) and the material for the tubes need to be approved for the pressure.

2.2 –Volume sampled and Flow rate during sampling

The detection limit obtained when using thermal desorption is proportional to the volume sampled, the larger volume sampled is the lowest the detection limit is. However, for a given analyte, there is a maximum volume that can be sampled before the analyte passes out the back end of the sorbent bed (breakthrough).

For each sorbent there is an optimal range of flow rates but a typical range is between 10 and 250 ml/min. If the flow rate is too high, the analytes wouldn´t have enough time to interact with the sorbent material and if the flow rate is too low, there is a risk of back-diffusion.

The volumes needed to reach the thresholds set in ISO14687-2 [2] for hydrocarbons, sulfur compounds and halogenated compounds have been estimated based on several assumptions:

Assumption 1: Quantification limit for the method

The quantification limit shall be less than or equal to the limits (also called threshold values) stated in the standard ISO14687-2. A criterion for acceptation is presented in ISO/CD 21087:2017 as: LOQ + uLOQ < limits in ISO14687-2.; for the calculation, uLOQ was estimated to be 50%. The instrument´s required limit of quantification is presented in table 1:

Table 1: instrument´s required limit of quantification based on assumption 1

Components	**Instrument´s required LOQ (µmol/mol)**
Total hydrocarbons (CH4 basis)	1
Total Sulphur compounds (H2S, COS, CS2 and mercaptans as a basis)	0.003
Total halogenated compounds (Hbr, HCl, Cl2 or organic halides)	0.03

Assumption 2: Limit of quantification for individual compounds

Very few documents treat the problematic of the LOQ for individual compounds in a family. However, this is somehow a bit similar to the problem of missing data. In this case, it is common to use the method of the replacement where every value below LOQ is replaced by a constant such as LOQ/2 (or LOQ/√2). In this case, the LOQ individual was chosen to be half of the LOQ for the total species (see table 2).

Table 2: *instrument´s required limit of quantification for individual compounds*

	µmol/mol	nmol/mol
Hydrocarbon (µmol C/mol)	0.5	500
Sulphur	0.0015	1.5
Halogenated	0.015	15

Assumption 3: Typical LOQs in thermal desorption

For the calculation, it was assumed that the LOQ for any compound in thermal desorption/GC is 2 ng.

Using the three assumptions, the volume of hydrogen to be sampled on sorbent tubes to reach the thresholds set in ISO14687-2 is presented in table 3 for the compounds that are studied in this task.

Table 3: Calculation of the volume of hydrogen to be sampled on sorbent tubes to reach the thresholds set in ISO14687-2

	nmol/mol	ml of hydrogen to sample
Methane	500	6
Ethane	250	6
Propane	160	7
Butanes	125	7
Acetone	160	5
Methanol	500	3
Ethanol	250	4
Octane	60	7
Decane	50	7
Dichloromethane	15	38
Tetrachloroethylene	15	20
Tetrachlorohexafluorobutane	15	11
Dichlorobenzene	15	22
Carbonyl sulphide	1.5	543
Carbon disulphide	1.5	429
Tert-butyl mercaptan	1.5	362
Tetrahydrothiophene	1.5	370
Methyl-mercaptan	1.5	679

Very small volumes need to be sampled for both hydrocarbons and halogenated hydrocarbons. However, due to the low threshold set for sulfur compounds, this volume is significantly higher for sulphur compounds.

2.3 - Storage

Sampled sorbent tubes should always be capped using ¼” brass Swagelok-type screw caps fitted with PTFE ferrules [3]. The tubes should always be stored in as clean an atmosphere as possible. As an additional precaution, the tubes can be wrapped in uncoated aluminium foil.

If the sorbent contains more than one sorbent, refrigeration is recommended to minimize risk of middle-volatility analytes migrating from weaker to stronger sorbents during storage.

2.4 – Transportation

It is recommended to use field (transport) blanks [4] that are transported with the tubes to be used for sample collection. Once at the sampling location, all the processes carried out on the sampling tubes (unwrapping, uncapping, recapping, rewrapping etc) except sample collection itself, should also be carried out on the field blanks. They provide important controls for all tube handling storage and transport procedures.

One great advantage of tubes is that they are small, convenient and readily transported. In many cases, regular postal service can be used [5].this recommendation when sampling air is most probably applicable also in the case of hydrogen as hydrogen will not be retained on the sorbent.

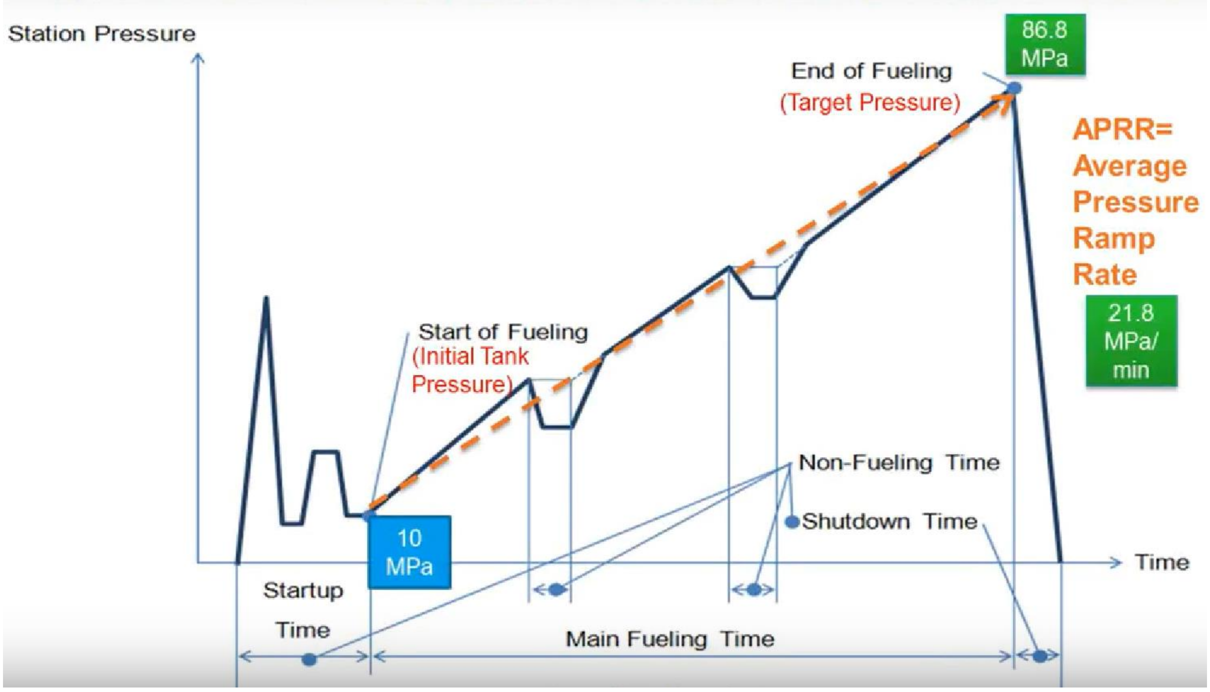
Tubes should be transported to and from the sampling location inside a dedicated storage container.

3 – Sampling points

According to ISO21087, samples should be collected at the HRS nozzle and be representative of the duration of the refuelling protocol. Transfer or sample from original vessel should be avoided to minimize risk of impurity losses as well as contamination. Thus, the transfer from the original vessel to sorbent tubes is not prohibited. However if transfer is performed, it shall be documented with relevant data like vessel type and time before and after transfer.

The transfer will require connecting a regulator to the original cylinder to reduce the pressure so as the pressures and flow are reasonable at the inlet of the sorbent tube. The sampling line must also include a mass flowmeter or a mass flow regulator to control the flow across the tube. The transfer must be performed safely. ISO21087 refers to ISO19880-1 Annex I regarding sampling strategies. A safety perimeter should be established preventing public access no closer than 8 meters as a default to the HRS sampling device and the ventilation assembly.

Taking samples on sorbent tubes directly at the nozzle is currently not an easy task. There is currently no implementation of sampling onto sorbent tubes at stations. A possibility would be to sample during the “pressure pulse” at the start of the refuelling as the volume of gas to sample on sorbent is relatively low. The startup phase of the refuelling ensures a safe connection between the nozzle and vehicle receptacle. The dispenser sends a startup connection pulse after verifying the coupling between the receptacle and the nozzle. The initial vehicle tank pressure is detected with an initial pressure pulse. A second pressure pulse is used to estimate the volume of the vehicle tank, and to detect any leaks. No more than 200 grams of hydrogen is allowed to flow into the HFCEV tank during this phase. However, to control precisely the volume on the tubes would be challenging.



**From presentation “An introduction to SAE Hydrogen Fueling Standardization, https://www.energy.gov/eere/fuelcells/webinar-introduction-sae-hydrogen-fueling-standardization*

In all cases, sampling from the nozzle on sorbent tubes will require extensive changes of the fueling process (otherwise, the control system of the dispenser will shut down) which may require manual sampling in maintenance mode, which is technically difficult to implement. A main limitation would be for the pressure reduction to lower than 10 bar. This operation will also require a stringent purging process afterwards to eliminate eventual contaminants (mostly air and water) that could be introduced due to change in the fueling process.

As a joint effort between IFE (MetroHyVe) and SINTEF (HYDRAITE), a meeting was held in 2018 to discuss the possibilities to combine sampling from the nozzle and sampling onto sorbent tubes. A concept making use of the hydrogen volume that is vented after sampling was discussed.

4 – Existing devices

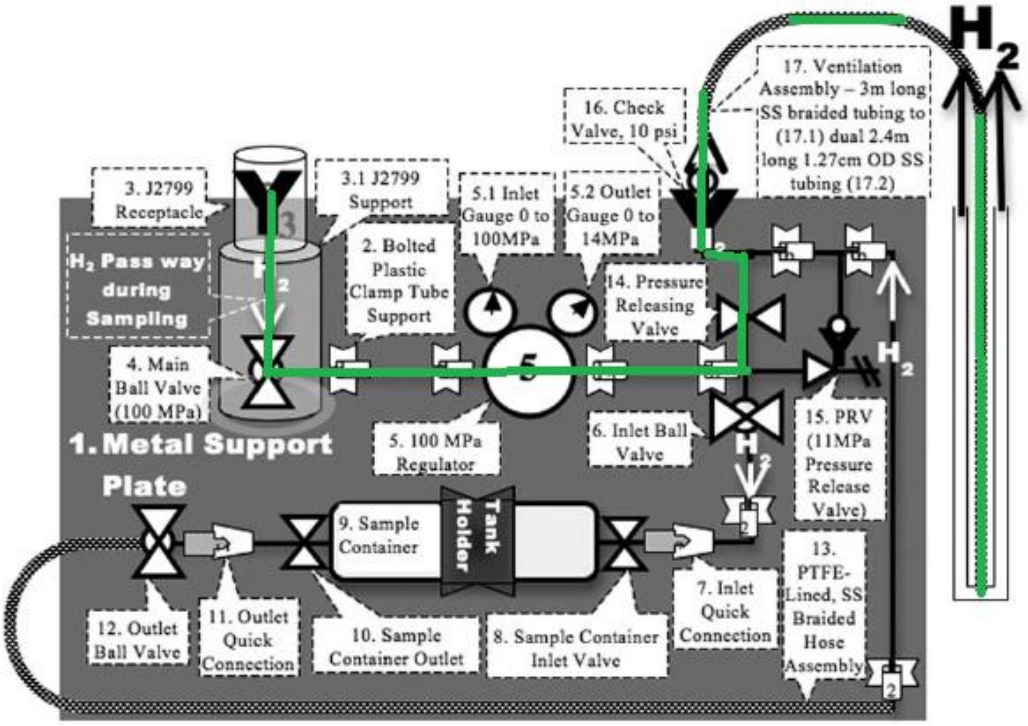
Argonne National Laboratory [6] has developed one strategy for detecting impurities in hydrogen. The strategy uses an enrichment device that employs a pressure-swing adsorption cycle. The sample passed through a bed of sorbents at high pressure so that the impurities are adsorbed on the sorbent surface. Releasing the pressure in the sorbent chamber then releases the impurities into the gas phase to elevate their concentrations in that space. The enrichment factor for each gas species depends on the sorbent and the gas species used in the pressure-swing enrichment device (typically more than one order of magnitude).

An email was sent to obtain more information on the sorbent used here; however no answer was received.

5 – Potential developments

5.1 – Series sampling device

Sampling on sorbent tubes could be performed using the series sampling device during the release of the pressure after sampling the cylinders.

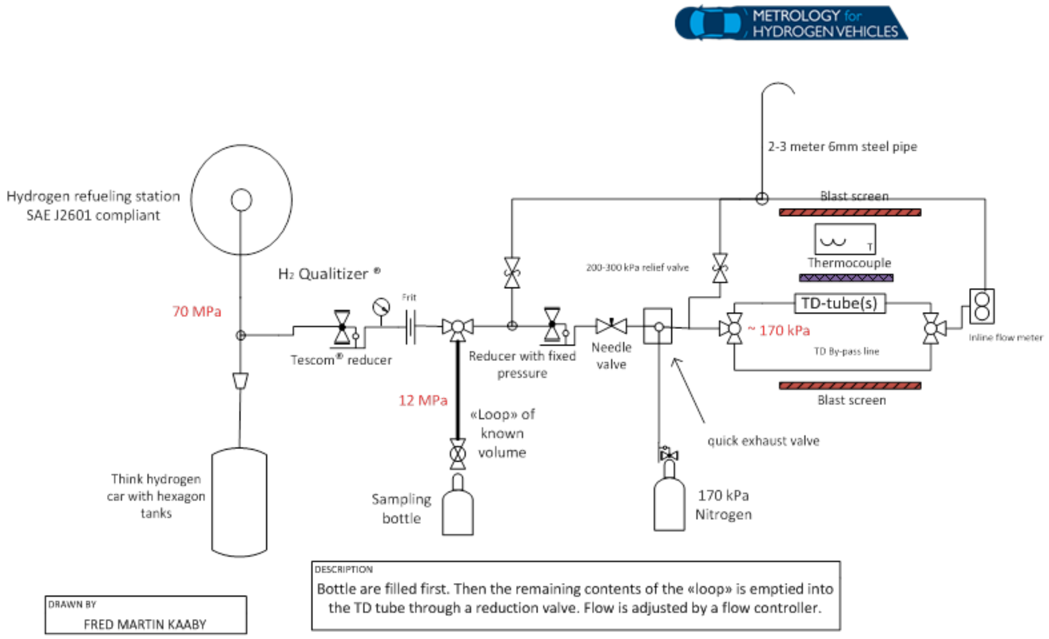


If a tee connector is added after the check valve (16), a part of the flow could pass through different sorbent tubes as long as a flowmeter (preferably a mass flow controller) is added to the new added line.

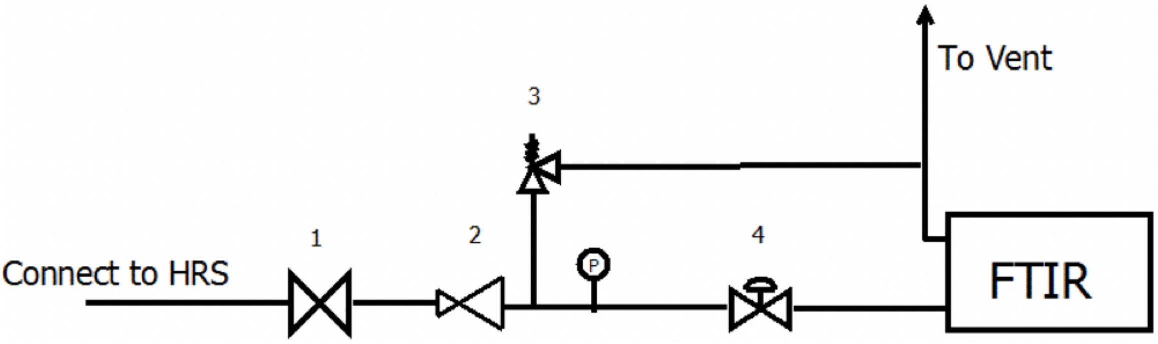
5.2 – Bleed when implementing online analysers

The implementation of online hydrogen fuel quality control has been investigated as part of the MetroHyVe project as the information from one or several sensors could provide valuable and direct information about the quality of the hydrogen dispensed.

A design for a bleed from HRS was created as part of the MetroHyVe and HYDRAITE joint effort. The design is presented in the following figure.



IFE designed a possible a high-pressure bleed that could be implemented at their station after the chiller. A pressure regulator would reduce the pressure to fit FTIR and GC-TCD instruments that could be installed and operated onsite. With this set-up, it is possible to adapt/control the volume of gas passing through sorbent tubes by adding flow controllers. Online analysis results could then be compared for some compounds to the results from the TD analysis.



1) Shut-off valve (Full HRS pressure rating)
2) Pressure reduction valve, target pressure 1-20 bar
3) Safety release valve
4) Needle valve to regulate flow to equipment

6 – Conclusions

It is currently not possible to directly sample on tubes at the nozzle of the HRS. Due to the fact that pressure needs to be reduced to a maximum of 10 bar before reaching the tubes, implementing sampling on tubes at the nozzle would be very challenging in many aspects including safety aspects.

However, two possibilities are presented in this report:

1) Making use of the hydrogen that is vented during current sampling procedures
2) Using the “pressure pulse” at the start of the refuelling

If the station is modified to accommodate the use of online analysers and/or sensors, this will also open the possibility to implement a design the sampling on tubes.

The transfer of hydrogen sample from the original vessel to sorbent tubes is not prohibited although this could risk impurity losses as well as further contamination of the sample. If the approach is taken, transfer is performed, it should be documented with relevant data such as vessel type, gas pressure and time before and after transfer. This is currently the best option for sampling hydrogen onto sorbent tubes.

7 – References

[1] Communication with Rachael Szafnauer from Markes International

[2] ISO 14687-2:2012, Hydrogen fuel – Product specification – Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles

[3] Markes International application note 005; Advice on sorbent selection, tube conditioning, tube storage and air sampling

[4] Markes International application note 019; Minimising artefacts – considerations for storage and transport of sorbent tubes

[5] Monitoring VOCs in Air using sorbent tubes followed by thermal desorption-capillary GC analysis: summary of data and practical guidelines, E. Woolfenden, Journal of the Air and Waste Management Association; 1997, 47,1, 20-36

[6] https://www.anl.gov/tcp/accurate-detection-of-impurities-in-hydrogen-fuel-at-lower-cost-anlin08072