Programme

- 9.30 Introduction to MetroHyVe project
- 9.45 Overview of the day
- 10.00 Gas sampling devices (overview)
- 10.30 Gas sampling vessels (overview)
- 11.00 Break
- 11.30 Particles sampling (overview)
- 11:45 Health and safety
- 12.05 Lunch
- 13.00 Head over to the hydrogen refuelling station for a visit

METROLOGY for HYDROGEN VEHICLES

Sampling vessels

Oliver Büker, Karine Arrhenius - RISE

Workshop on Hydrogen sampling training course
12th of March 2020, Delft, The Netherlands

EMPIR EURAMET

This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

Overview

- Parameters to consider when selecting a sampling vessels for H2
- State-of-art for commercially available sampling cylinders
- Developed procedure to prepare cylinders before sampling
- Other types of vessels: sorbent tubes
- Available resources

Vessels for sampling hydrogen

- Must be cleaned and evacuated before sampling
- No loss of impurities during transportation (Timeline: 2-4 weeks maybe even longer if from USA)
- Sampling hydrogen may imply the presence of several species at the same time
- Vessels need to be approved for transportation
- Vessels need to be compatible with available H2-sampling devices developed to take samples at HRS stations

Component	ISO 14687 -2 µmol/mol	ISO 14687 (new) EN 17124 µmol/mol
Helium	300	300
Nitrogen	100	300
Argon	100	300
Methane	/	100
Oxygen	5	5
Carbon dioxide	2	2
Carbon monoxide	0.2	0.2
Water	5	5
Total Hydrocarbons (non methane)	2	2
Total Sulfured compounds	0.004	0.004
Ammonia	0.1	0.1
Formaldehyde	0.01	0.2
Formic acid	0.2	0.2
halogenated compounds	0.05	0.05

from **INTERNATIONAL WORKSHOP METROLOGY FOR SUSTAINABLE HYDROGEN ENERGY APPLICATIONS, Martine Carré, Air Liquide**

Sampling approach: risk analysis

- A false positive (over-estimation) would be the case where the hydrogen is sufficiently pure but the sampling procedure itself contaminated the sample. Examples of this would be an air leak in the system allowing ingress of oxygen and nitrogen into the hydrogen sample or presence of contaminants in the vessels before sampling: Need for proper preparation of the vessels before sampling

- A false negative (under-estimation) would be the case where impurities in the hydrogen are lost either during the sampling or transport of the gas sample vessel. An example of this could be hydrogen sulphide which may adsorb to stainless steel walls (such as in the sampling device or sampling vessel) and therefore would be lost or significantly reduced in the sample upon reaching the laboratory: need to select the proper cylinder material

State-of-art of sampling vessels

- Among the characteristics for the fuel specification listed in standard ISO14687-2, several species are reactive (e.g. halogenated compounds, ammonia, formaldehyde, formic acid, carbon monoxide) and/or may adsorb onto solid media such as cylinder walls (e.g. water).

- Therefore, it must be ensured that adequate sampling vessels are used for these species to avoid losses occurring while the sample of hydrogen is collected at the HRS station and transported to the laboratory. Losses within the vessels would lead to falsely lower levels of impurities being measured than are present in the original hydrogen

Parameters to take into account while choosing a cylinder to sample hydrogen

- Size (e.g. 10 L: the volume must be enough to perform all required analyses)
- Configuration: two ended cylinders, one ended cylinders
- Materials (Aluminium, steel, alloys and composite materials)
- Different inner treatments as passivation
- Compatibility with available H2-sampling devices (Limiting factor for now)
- Pressure requirements (to be certified for at least 100 bar or the sampling pressure)
- Price range

State-of-art for commercially available sampling vessels - cylinders

Multitude of methods used to passivate the internal surface of cylinders but no great deal of detail about these technologies (proprietary information). The treatments are often to make the surface inert to targeted compounds. Passivation is a technique used to occupy the active areas on the surface of a vessel.

Three categories of treatment can be distinguished:

1) Cleaning, polishing of the internal surface (electro) chemically or mechanically

2) Chemical treatment without targeting structural change of the surface

3) Multi-molecular layer coverage of the initial surface

State-of-art for commercially available sampling vessels - cylinders

Several researchers or cylinder providers have performed tests to assess the stability of the reactive impurities in different vessels show:

1) Often comparison of cylinders with and without passivation

2) Tests performed under different conditions (pressure…), using different vessels sizes and configurations, different matrices (mostly air and rarely hydrogen), concentrations often largely above the threshold values (ISO14687 standard)

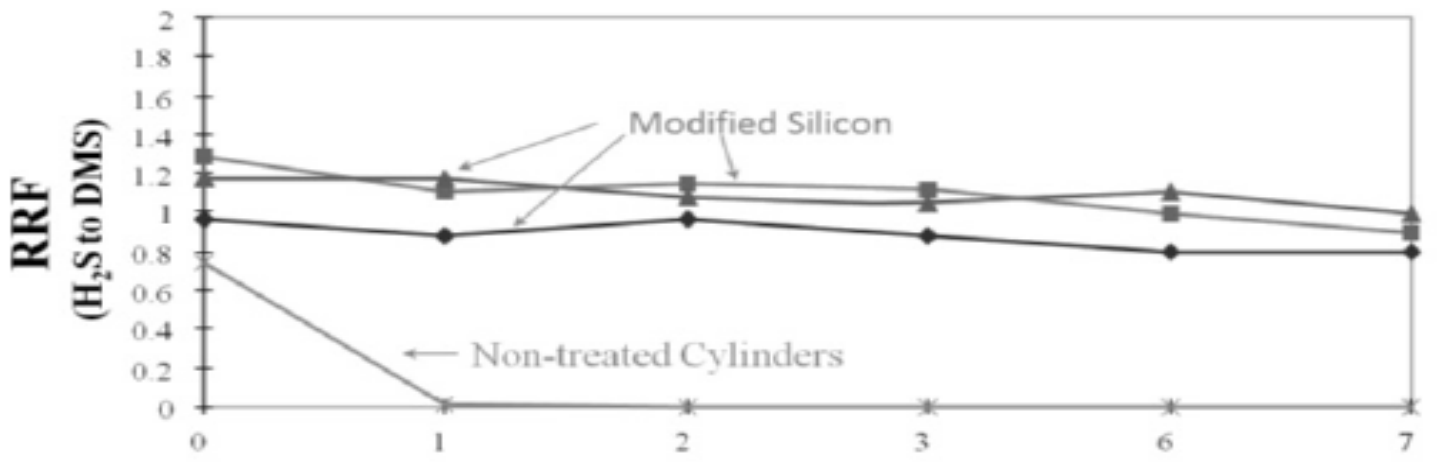
3) Information about tests conditions are often incomplete, therefore difficult to compare different studies

4) Sulphur compounds (specifically H2S) have been studied in larger extends than formaldehyde and formic acid.

State-of-art for commercially available sampling vessels - cylinders

Most of the results (in aluminium or steel cylinders) show that some kind of passivation is required when storing impurities as sulphur compounds and ammonia (at least).

It is therefore of high importance to perform stability tests on these impurities in chosen cylinders and at the conditions relevant for the sampling of hydrogen in order to ensure that these cylinders are suitable for transporting the reactive impurities in hydrogen that need to be analysed for ISO 14687 hydrogen purity.



Steel

H2S at 17 ppbv in SilcoNert®2000-coated cylinders versus uncoated stainless steel cylinder [1]

[1] Characterizing the performance of surface modifications that enhance sensitivity, reliability, reproducibility and accuracy of analytical instruments", SilcoTek notes, G. Barone, D.Smith, M. Higgins

State-of-art for commercially available sampling vessels - cylinders

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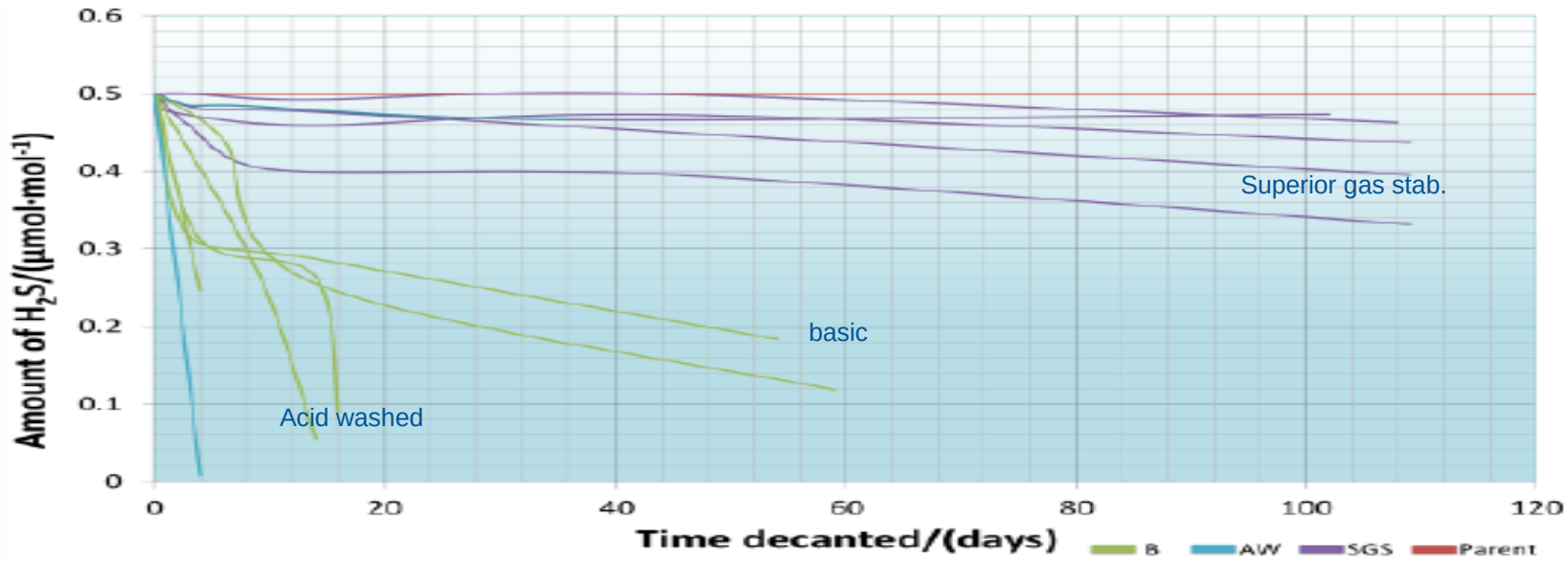


Aluminium

H2S amount fraction vs time [2]

[2]The effect of internal surface finish of aluminium alloy cylinders on the stability of sensitive gas mixtures", A. Lomax, G. Squire, Gas Analysis conference 2017

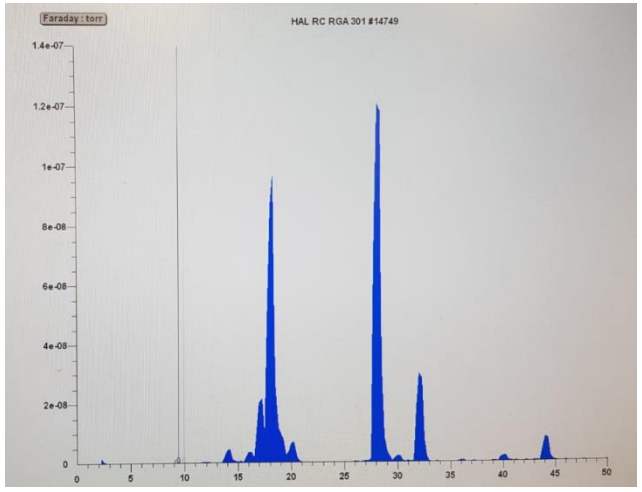
Procedure for preparing vessels before sampling

The procedure includes the following steps:

- Prior to attaching a cylinder to the evacuation rig, blow down the cylinder in a fume cupboard or extraction vent until empty, then close the cylinder valve when at atmospheric pressure.
- Connect cylinder to evacuation rig using an appropriate cylinder valve connector.

If other cylinders are already on the evacuation rig, the cylinder valves of each of them must be closed before starting the evacuation of any additional cylinders

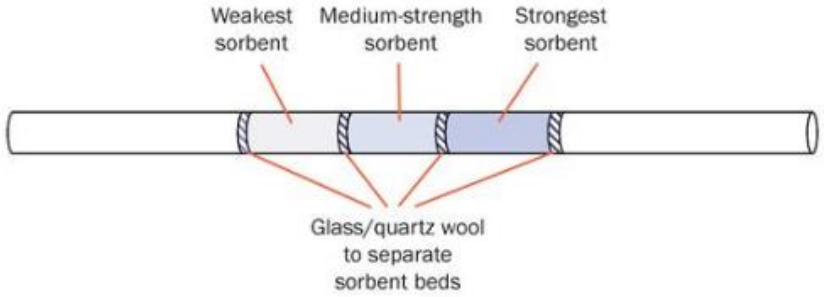
- Use the roughing pump to partially evacuate the cylinder prior to opening the turbo pump.
- Once the pressure in the vessel is at around 1.1 x 10^{-1} mbar or less, activate the turbo pump.
- Once at a suitable vacuum turn on the residual gas analyser to monitor outgassing of air, moisture and any remaining contaminants.
- Allow cylinder vacuum to reach 1 x 10^{-7} mbar.
- Monitor impurities on the residual gas analyser (Figure 4), if an expected impurity remains within the system this should be removed by heating or including a subsequent hydrogen purge step.



Other types of vessels: sorbent tubes

Adequate for the organic compounds included in ”total species” (sulphur, hydrocarbons, halogenated)

Many sorbent materials available
classified by strength + combination of sorbents



Easy to transport as the hydrogen will not be retained

Combined with gas chromatographic techniques: will then give information on which compounds are actually present in the gas

Stability studies on tubes - results

METROLOGY for HYDROGEN VEHICLES

Table 6. Recovery yield obtained for hydrocarbons on 3 different sorbent tube.

	Chromosorb 106		TCC		Tenax TA	
	Recovery (%)	Rel. Standard Deviation	Recovery (%)	Rel. Standard Deviation	Recovery (%)	Rel. Standard Deviation
Propane	91.3	2.1	95.0	1.0	9.9	49.9
Isobutane	96.5	0.7	88.3	1.9	20.4	15.0
Butane	97.5	0.4	96.3	1.4	61.3	24.6
Ethanol	102.1	7.2	145.9	36.6	81.0	1.3
Isopentane	95.9	0.4	85.4	0.8	54.0	8.6
Acetone	91.9	5.0	51.4	6.9	55.3	6.1
Pentane	95.1	0.7	93.1	1.4	87.9	3.3
Heptane	97.6	5.4	97.7	3.6	91.9	6.3
Decane	92.8	2.5	98.4	4.1	91.5	4.2

Stability studies on tubes - results

Figure 1. Storage stability of hydrocarbons on Chromosorb 106. (**a**) for butane, propane, isobutane, decane, ethanol; (**b**) for pentane, isopentane, acetone and heptane.

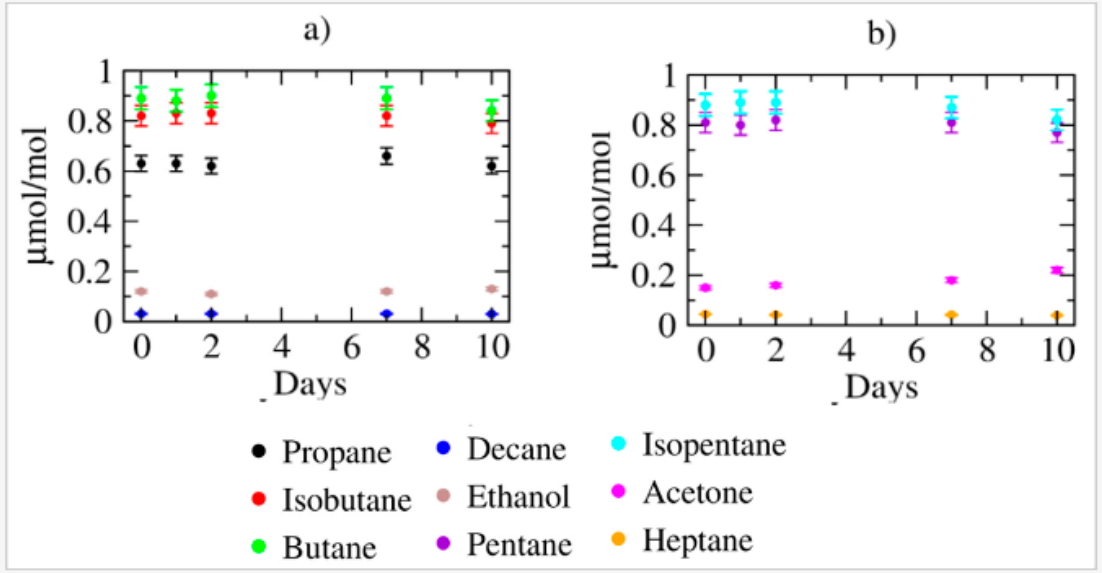
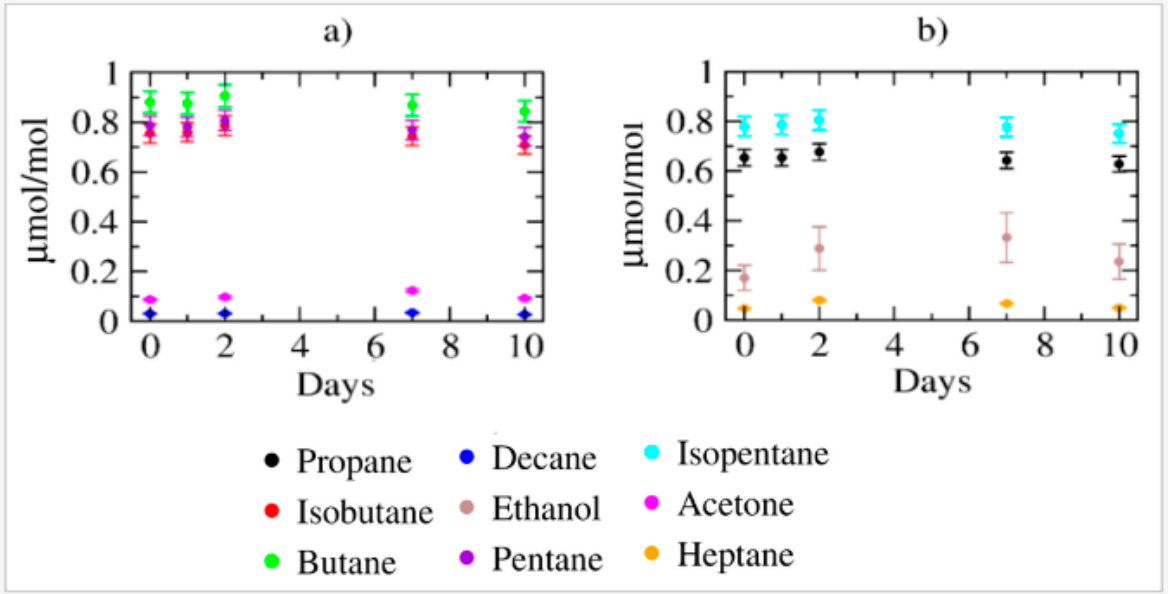


Figure 2. Storage stability of hydrocarbons on TCC. (**a**) for butane, acetone, isobutane, decane, pentane; (**b**) for propane, isopentane, ethanol and heptane.



	BP (°)	Chromosorb 106		TCC		Tenax TA		Carboxen 1003		Tenax TA/Sulficarb	
		Recovery yield	Storage stability	Recovery yield	Storage stability	Recovery yield	Storage stability	Recovery yield	Storage stability	Recovery yield	Storage stability
Propane	-42	Very good	Very stable	Very good	Very stable	Not suitable	Unstable	n.d.	n.d.	n.d.	n.d.
Isobutane	-11	Very good	Very stable	Good	Very stable	Not suitable	Very Stable	n.d.	n.d.	n.d.	n.d.
Butane	0	Very good	Very stable	Very good	Very stable	Low	Relatively Stable	n.d.	n.d.	n.d.	n.d.
Ethanol	78	Very good	Very stable	Not suitable	Unstable	Low	Relatively Stable	n.d.	n.d.	n.d.	n.d.
Isopentane	28	Very good	Very stable	Good	Very stable	Low	Relatively Stable	n.d.	n.d.	n.d.	n.d.
Acetone	56	Very good	Unstable	Low	Very stable	Low	Unstable	n.d.	n.d.	n.d.	n.d.
Pentane	36	Very good	Very stable	Very good	Very stable	Good	Very stable	n.d.	n.d.	n.d.	n.d.
Heptane	98	Very good	Very stable	Very good	Very stable	Very good	Very stable	n.d.	n.d.	n.d.	n.d.
Decane	174	Very good	Very stable	Very good	Very stable	Very good	Very stable	n.d.	n.d.	n.d.	n.d.
Chloromethane	-26	Not suitable	n.d.	Low	Relatively Stable	Not suitable	n.d.	n.d.	n.d.	n.d.	n.d.
Vinylchloride	-14	Not suitable*	Very stable	Not suitable*	Unstable	Low	Very Stable	n.d.	n.d.	n.d.	n.d.
freon 113 (trichloroethane)	47	Very good	Very stable	Very good	Relatively Stable	Not suitable	Very Stable	n.d.	n.d.	n.d.	n.d.
dichloromethane	40	Very good	Very stable	Very good	Unstable	Good	Very Stable	n.d.	n.d.	n.d.	n.d.
12-dichloroethylene	55	Very good	Very stable	Very good	Relatively Stable	Good	Very Stable	n.d.	n.d.	n.d.	n.d.
chloroform	61	Low	Very stable	Low	Unstable	Low	Very Stable	n.d.	n.d.	n.d.	n.d.
Trichloroethylene	87	Good	Very stable	Very good	Very Stable	Very good	Very Stable	n.d.	n.d.	n.d.	n.d.
12-dichloropropane	97	Very good	Very stable	Very good	Relatively Stable	Very good	Very Stable	n.d.	n.d.	n.d.	n.d.
112-trichloroethane	114	Good	Very stable	Very good	Relatively Stable	Very good	Very Stable	n.d.	n.d.	n.d.	n.d.
tetrachloroethylene	121	Very good	Very stable	Very good	Relatively Stable	Very good	Very Stable	n.d.	n.d.	n.d.	n.d.
Tetrachloro hexafluorobutane	135	n.d.	n.d.	Very good	Relatively Stable	Very good	Very Stable	n.d.	n.d.	n.d.	n.d.
1,2-Dichlorobenzene	180	n.d.	n.d.	Very good	Very stable	Very good	Very Stable	n.d.	n.d.	n.d.	n.d.
Carbonyl sulfide	-50	n.d.	n.d.	n.d.	n.d.	Very good	Not stable	Very good	Very stable	Very good	Not stable
Carbon disulfide	46	n.d.	n.d.	n.d.	n.d.	Very good	Very stable	Very good	Not stable	Very good	Not stable
tert-butyl mercaptan (T-BM)	64	n.d.	n.d.	n.d.	n.d.	Low recovery	Very stable	Very good	Not stable	Very good	Not stable
Tetrahydrothiophene (THT)	119	n.d.	n.d.	n.d.	n.d.	Very good	Very stable	Very good	Not stable	Very good	Very stable

Sampling points for tubes?

According to ISO21087, samples should be:

1) collected at the HRS nozzle
2) be representative of the duration of the refuelling protocol
3) Transfer or sample from original vessel should be avoided to minimize risk of impurity losses as well as contamination.

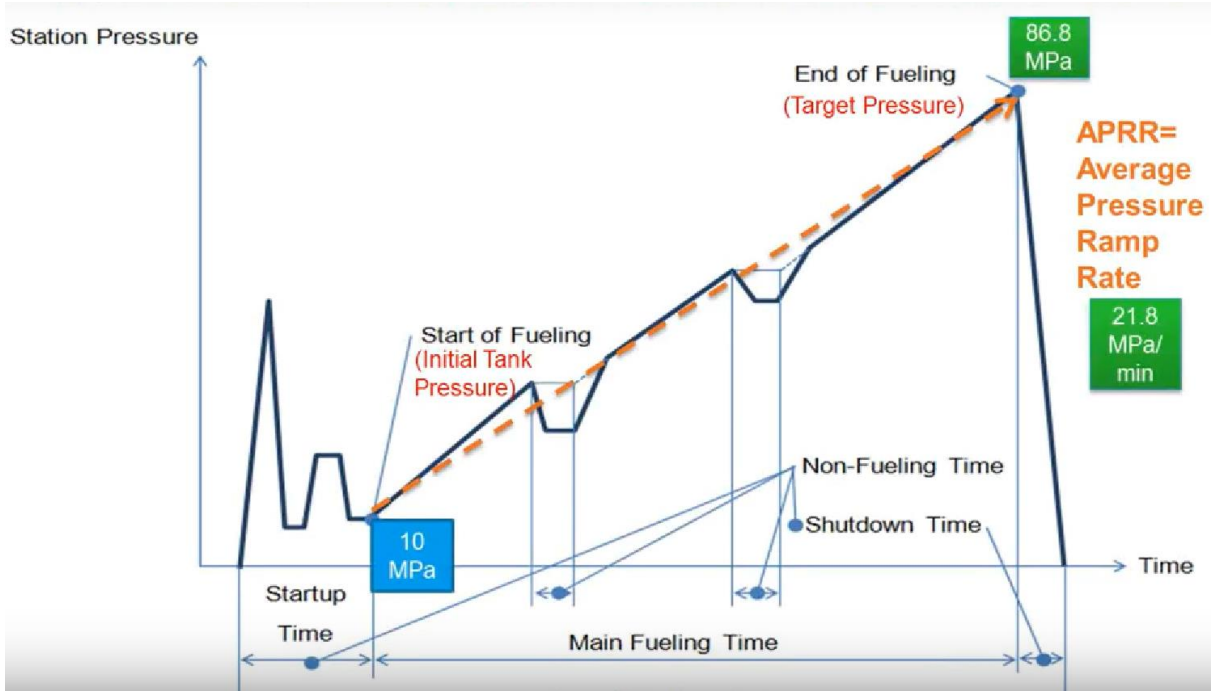
Thus, the transfer from the original vessel to sorbent tubes is not prohibited. If transfer is performed, it shall be documented with relevant data like vessel type and time before and after transfer.

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. (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).

Sampling points for tubes?

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 start-up phase of the refuelling ensures a safe connection between the nozzle and vehicle receptacle. The dispenser sends a start-up 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

Transportation back to the laboratory

Hydrogen is legally classified as dangerous to transport by the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR), in the International Regulations Concerning the Carriage of Dangerous Goods by Rail (RID), International Maritime Dangerous Goods (IMDG) and the International Air Transport Association (IATA). The hazards associated with the handling of hydrogen are fire, explosion and pressure, so the transport of the sample must be based on existing legislation to avoid and prevent risk and exposures.

The hydrogen UN number is 1049 and its United Nations Transport Officer Designation is “HYDROGEN COMPRESSED”. The transportation hazard Class is class 2 and the label must be 2.1 (flammable gas) and GHS 04 (compressed gas).

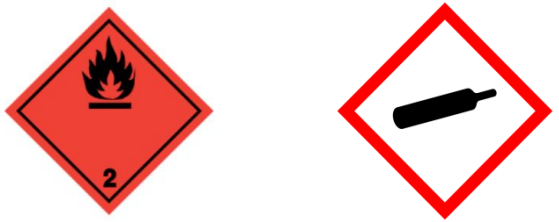


Figure 1. Label 2.1 (left) and GHS 04 (right).

Transportation back to the laboratory

Each sample must be individually coded. This coding shall allow the traceability of the sample during the transport, storage and analysis process.

All essential information for the laboratory will be indicated on a label on the containers. These labels shall be securely affixed to the sample containers, but shall not hinder their use. The information given shall preferably include:

- The number of the container;
- The type of container;
- The place where the sample was taken;
- All the information necessary for the identification of the sampled carcase;
- The date and time; or the period of sampling;
- Sample procedure;
- The actual destination of the container;
- Any maintenance required on the container (e.g. leaks);
- Any useful information for the analytical laboratory concerning the sample;
- The pressure of the sample, if the vessel does not incorporate a manometer;
- The pressure in the reservoir;

Copies of other relevant documents relating to the nature of the sample (safety data sheets, technical specifications, etc.) and the ADR Transport document (delivery note) or similar may be attached.

Available resources

Reports are available on the project website www.metrohyve.eu

A4.4.1: Literature review – state-of-art for the storage of reactive species in vessels

A4.3.1: Review and selection of 3-5 compounds per family of total halogenated, total sulphur and total hydrocarbons

A4.3.2: Literature review – state of art of sampling and storage of compounds selected in A4.3.1

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

A4.1.7: Good Practice Guide on effective sampling and transportation of hydrogen from the refuelling station as required by ISO14687

Applied Sciences, Appl. Sci. **2020**, 10(1), 120; https://doi.org/10.3390/app10010120
Hydrogen Purity Analysis: Suitability of Sorbent Tubes for Trapping Hydrocarbons, Halogenated Hydrocarbons and Sulphur Compounds

THANK YOU

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