METROLOGY for HYDROGEN VEHICLES

REPORT:

D8

A4.4.5: Good practice on the suitability of vessels and gas cylinders for sampling hydrogen as required by ISO14687

16ENG01 MetroHyVe

Lead Partner: RISE Research Institutes of Sweden AB

Due date: 31/03/2020

Actual submission date: 20/04/2020

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This report was written as part of activity A4.4.5 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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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.

Contents

1 - Introduction

While selecting a vessel for sampling hydrogen, several parameters must be considered:

- The vessels must be cleaned and evacuated before sampling
- No loss of impurities shall occur during transportation (Timeline: 2-4 weeks maybe even longer if e.g. transported to Europe from USA or Asia)
- Sampling hydrogen may imply the presence of several species at the same time; it must be ensured that the vessel(s) is/are suitable for all impurities
- The vessels need to be approved for transportation
- The vessels need to be compatible with available hydrogen sampling devices developed to take samples at Hydrogen Refuelling Stations (HRSs)

Decision about the suitability of a specific vessel for hydrogen sampling must consider all these parameters. The most restrictive parameter is the compatibility of the vessels with the sampling device. Currently, mainly three sampling devices are in use: the European variant for parallel sampling according to ISO19880-1, annex I [2] using a Qualitizer and a 10 l cylinder, the US variant for series sampling according to ASTM D7606:1 [3] and the Japanese variant. All the sampling devices require a gas cylinder as sampling vessel.

Among the characteristics for the fuel specification that are listed in the standard ISO14687 Grade D [1] (or revision of the standard), 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 reactive species to avoid losses occurring while the sample of hydrogen is collected at the HRS 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.

Several researchers or cylinder providers have performed tests to assess the stability of the reactive impurities in different vessels. The studies mostly focused on comparison of cylinders with and without passivation. The tests were performed under different conditions such as varying filling pressure, different vessels sizes and configurations, in different matrices (mostly air and rarely hydrogen, and at concentrations often largely above the thresholds values from the ISO14687 standard. As information about the tests conditions are often incomplete, it is difficult to compare the results from different studies to establish the suitability of a tested vessel for hydrogen sampling. It is also worth noticing that sulfur compounds (specifically H_2S) have been the subject of many studies while very little information is available for formaldehyde and formic acid.

In this report, we summarize the results of these studies and we present results from short-term stability tests performed during the course of the MetroHyVe project.

Finally, even if the focus of the report is on the suitability of gas cylinders for sampling hydrogen, the possibility to use other types of vessels, for instance sorbent tubes, is discussed in a sub-section of this report.

2 – Selection of the vessel material, configuration and surface treatment

There are many providers of sampling cylinders and many cylinders types. An exhaustive list of providers is given in MetroHyVe report A4.4.1 "Literature review – state-of-art for the storage of reactive species in vessels" [4]. It is important to underline that the choice of the cylinder (size, material, working pressure and temperature) should be properly addressed. The choice of the other parts of the sampling line must also be properly addressed but is not the subject of this report.

Parameters to address are:

- Compatibility with available H_2-sampling devices (Limiting factor currently)
- Price range
- Volume: the volume must be enough to perform all required analyses. According to MetroHyVe report A4.1.2 "Recommendations regarding the conditions for sampling at the HRS" [5], depending on analytical methods, the total volume of gas required by the labs to perform the whole sets of analyses to assess the purity of hydrogen according to ISO14687-2 varied from 20 Nlitres to almost 200 Nlitres. The volume of hydrogen sampled is dependent upon the volume of the vessel and the filling pressure.
- Pressure requirements (to be certified for at least 100 bar or the sampling pressure) and compatibility with the sampling device.
- Configuration: two-ended cylinders, one-ended cylinders, depends also mostly on the sampling device; The use of double-ended cylinders allows more flexibility as for example for purging the cylinder before sampling, but these cylinders are not yet compatible with the European sampling device. Some manufacturers also now developed cylinders with a dip tube fitted internally to a dual port valve which allows a purge of the cylinder.
- Materials: cylinders are made of different materials. The most common materials used today are aluminium, steel, alloys and composite materials. The cylinder valve must also be suitable (in particular the valve sealings)
- Different inner treatments as passivation; this parameter is of high importance to avoid loss of impurities by adsorption onto the inner walls of the cylinder.

Studies performed on sulfur compounds and ammonia lead often to the same conclusion: Cylinder passivation is required when storing these impurities.

There are a multitude of different methods developed for different applications (gases and/or concentration ranges) used to passivate the internal surface of cylinders. A variety of treatments exists to fit different applications. The treatments are often designed to make the surface more inert to targeted compounds. However, as most of these technologies remain proprietary information, not a great deal of detail is known about these technologies [6]. 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

2.1 – Treatment of stainless-steel cylinders

It is well known that stainless steel vessels are prone to absorbing sulfur compounds onto the surface.

SilcoNert passivation technique bonds an inert silica layer onto the surface of stainless steel, preventing reactive compounds from reacting with or adsorbing to the steel. SilcoNert can also be applied to glass, high temperature alloy (for instance nickel and chrome-containing alloys) or ceramic parts. SilcoNert®2000 is SilcoTek´s tradename for silicon chemical vapor-deposited (CVD) coating. SilcoNert 1000 is pure amorph silicon coating. The SilcoNert 2000 (also known as Sulfinert) coating has the SilcoNert 1000 coating as a base layer. This base layer is then functionalized with hydrogen carbon molecules to get better inertness and hydrophobicity.

Dursan is SilcoTek´s tradename for a carboxysilane coating. SilcoTek® Dursan® is a proprietary, patent pending, coating designed to improve the inertness, durability, fouling and corrosion resistance. The coating can be applied to stainless steel tubing and stainless-steel fittings but also valves, sample cylinders, regulators, fritted filters, mass flow controllers etc... Diverse materials can be coated: stainless steel, glass, ceramics, most steel alloys and super alloys. In many application notes, Dursan coating is described as a good alternative for ppmv level of reactive species while SilcoNert-coating is more commonly used for ppbv levels of reactive species.

SilcoTek described the different coatings in Table 1 [7]:

Table 1 – Overview of different available coatings

Coating types	Fluoropolymers (PTFE, PFA)	Silicon based (Sulfinert, SilcoNert)	Carboxysilane (Dursan)
General characteristics	Very inert Very corrosion resistant Poor adhesion Poor wear resistance	Very inert Great adhesion No carryover Good corrosion resistance Poor wear resistance	Good inertness Great adhesion No carryover Good corrosion resistance Good wear resistance
Max Temperature	260°C	450°C	450°C
Min Temperature	-240°C	-196°C	-100°C
Low pH limit	0	0	0
High pH limit	14	7	14
Thickness	25 µm	0.12 to 0.5 µm	0.5 to 1.5 µm
Chemical inertness properties [8]			
H_2S and sulfur compounds	-	Excellent	Excellent
Ammonia	-	Good	Fair

There are other companies providing passivation treatments such as Silonite (Entech Instruments Inc.).

2.2 - Treatment of Aluminium cylinders

All aluminium surfaces [6] that have been in contact with air are well passivated due to the development of an oxide layer. By increasing the thickness of this oxide layer, inertness can be improved. However, aluminium oxide has an inherent, honeycomb like structure. These are small

cavities in the nm range. Most of the reactions that take place on the internal surface of an aluminium cylinder are not direct reactions with the aluminium (oxide) surface, they are cavity enhanced reactions catalysed by the aluminium oxide structure.

Several cylinders providers have developed passivation treatments to increase the performances of aluminium cylinders, for example cylinders called SGS (Superior gas stability). According to Luxfer, the SGS interior is achieved by processing a cylinder through a series of proprietary, time-sensitive manufacturing operations that produce a consistent, better-performing internal surface.

Some information about the Performax treatment developed by EffecTech can be found in the application notes, report, presentations and papers on the EffecTech website. The Performax treatment applied to aluminium cylinders targets the microstructure by filling up the active sites at the nm level.

The cylinders mentioned above have been tested and have shown to improve the storage stability of reactive impurities such as H_2S (tested in SGS cylinders).

3 – Short-term stability studies performed during MetroHyVe

Short-term stability studies were undertaken as part of the MetroHyVe project. The studies were performed on gas mixtures containing two impurities and at levels of concentration that are relevant for hydrogen purity testing.

Test 1: The suitability of a SilcoNert 2000-treated stainless-steel sampling vessel and of an Aculife IV-treated aluminium sampling vessel was tested with a hydrogen gas mixture containing 100 ppb HCl and 100 ppb CO or 400 ppb HCl and 400 ppb CO. Tests were carried out at VSL.

Table 2 – Overview of the prepared and analysed mixtures at VSL (all hydrogen matrix containing 2-8% N_2)

	CO (ppb)	HCl (ppb)	Cylinder	Preparation date
VSL445051	104	103	5L Aculife IV aluminium	2 December 2019
VSL202035	106	104	3.6 L Silconert 200 coated Stainless Steel	2 December 2019
VSL526712	403	399	5L Aculife IV aluminium	29 November 2019

Test 2: The suitability of a Spectraseal-treated aluminium sampling vessel (called in the figures 2698) and of an untreated aluminium sampling vessel (called in the figures LUX0012) was tested with a hydrogen gas mixture containing 40 ppb H_2S and 110 ppb CO. Tests were carried out at NPL.

Test 3: The suitability of a Dursan, a Sulifnert and an untreated stainless-steel sampling vessel (1 litre) was tested with a hydrogen gas mixture containing around 40 ppb H_2S and 110 ppb CO from Test 2. Tests were performed 6 months after the preparation of the mixture. These tests were carried out at RISE.

The results are presented on the following figures and tables:

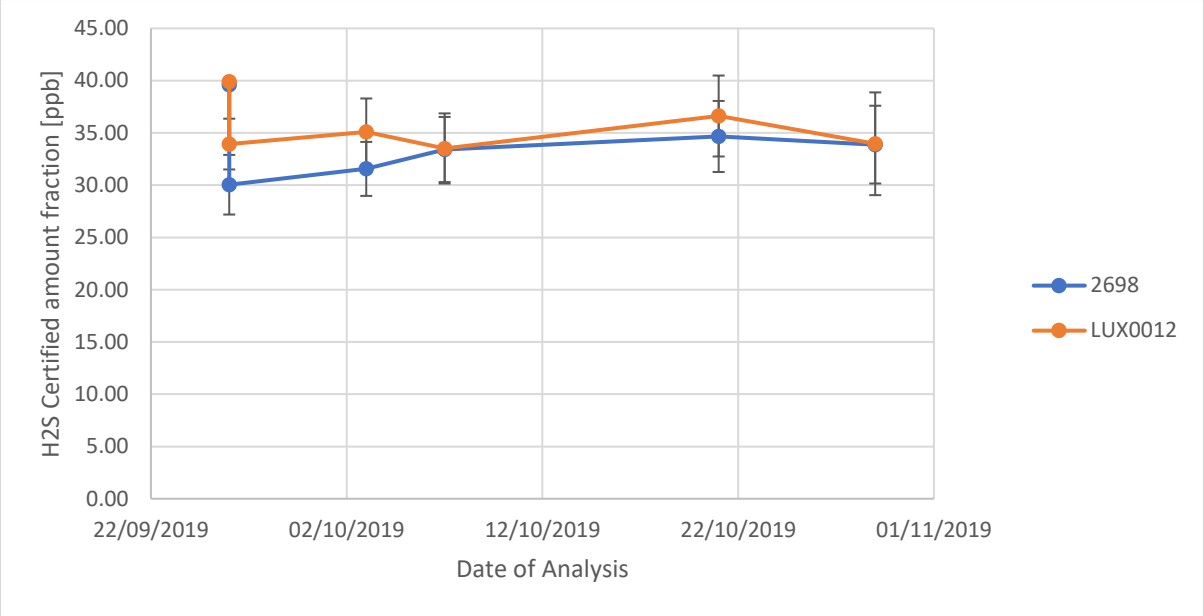

Figure 1: Short-term stability study for H_2S at 40 ppb in H_2 (Spectraseal-treated aluminium sampling vessel (2698) and untreated aluminium sampling vessel (LUX0012)) – Test 2

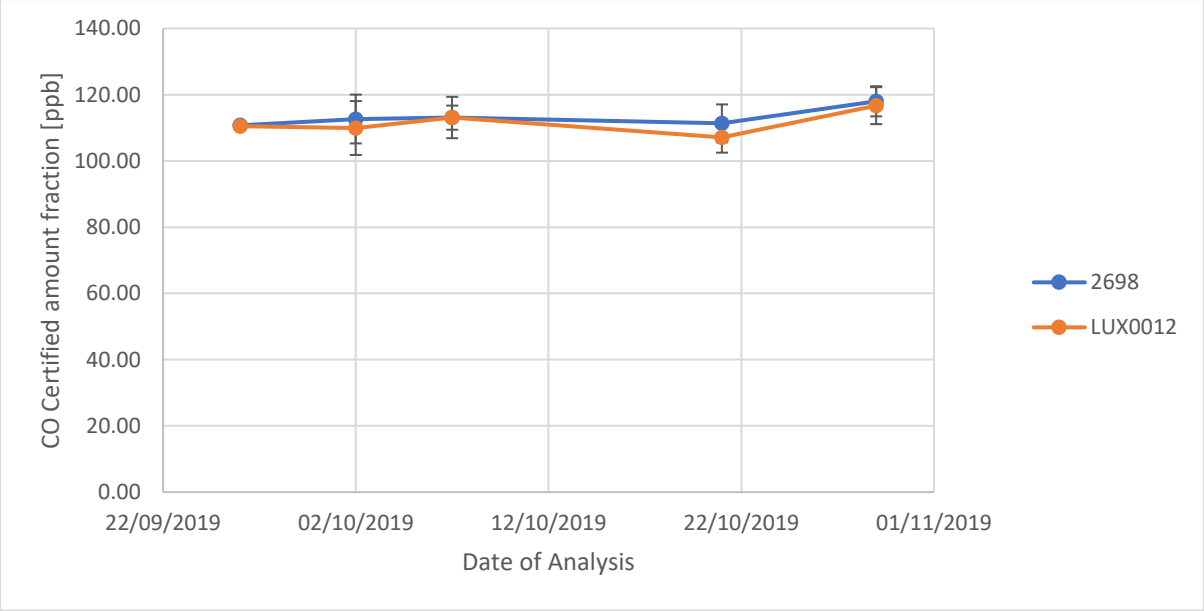

Figure 2: Short-term stability study for CO at 110 ppb in H_2 (Spectraseal-treated aluminium sampling vessel (2698) and untreated aluminium sampling vessel (LUX0012) – Test 2

For H_2S, the results show that there is a significant initial loss upon collection in both types of sampling vessel. Following this initial loss, the amount fraction of H_2S remains stable in both types of sampling vessel over the test period (5 weeks).

For CO, the results show that the amount fraction remains stable in both types of sampling vessel over the test period (5 weeks).

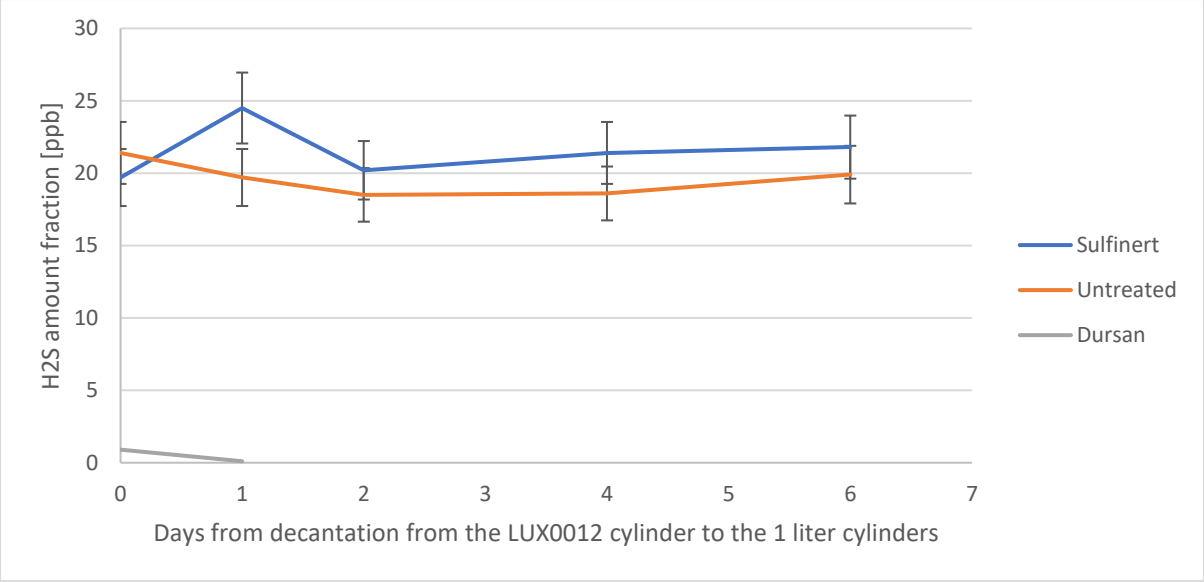

Figure 3: Short-term stability study for H_2S at around 40 ppb in H_2 after decantation to 1 litre stainless-steel cylinders) – Test 3

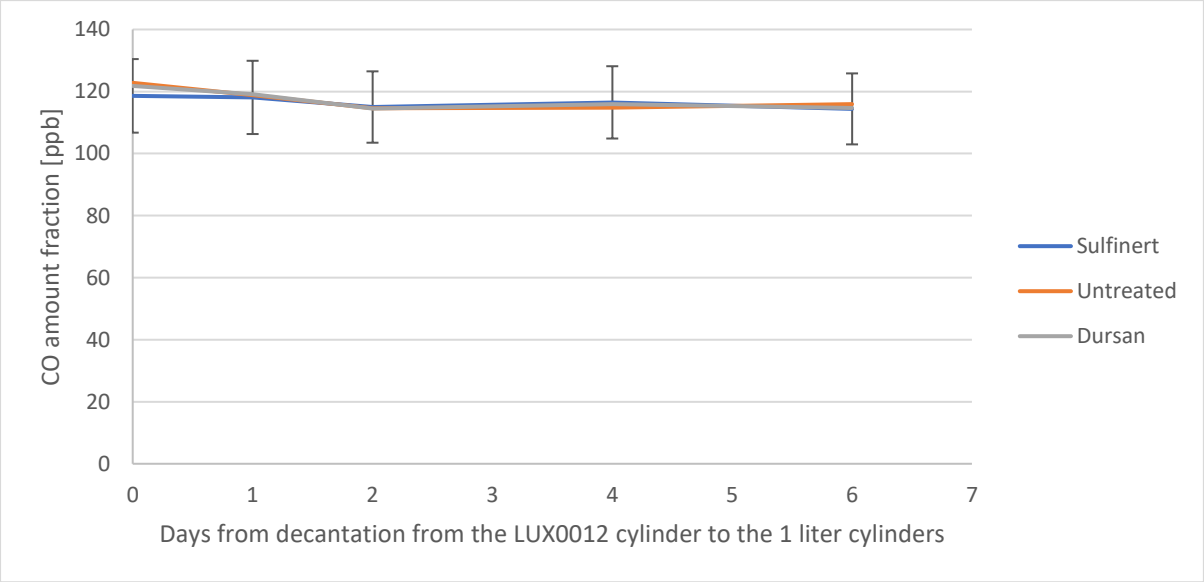

Figure 4: Short-term stability study for CO at 110 ppb in H_2 after decantation to 1 litre stainless-steel cylinders – Test 3

For H_2S, the results show that there is an almost total loss upon decantation into the Dursan cylinder while the amount fraction of H_2S remains stable in both untreated and Sulfinert cylinders for a period of at least 6 days after decantation. The concentration (22-24 ppb, Figure 3) at D0 (the day of decantation, 2020-03-10) in these cylinders is clearly lower than the concentration measured in the original cylinder (34 ppb, the 2019-10-29, Figure 1). However, almost 6 months separated these measurements.

For CO, the results show that the amount fraction of CO remains stable in the three types of 1 litre stainless-steel sampling vessels over a period of at least one week. The concentration (118-120 ppb, Figure 4) at D0 (the day of decantation, 2020-03-10) is close to the concentration measured in the

original cylinder (117 ppb, the 2019-10-29, Figure 2) even if 6 months separated these two measurements.

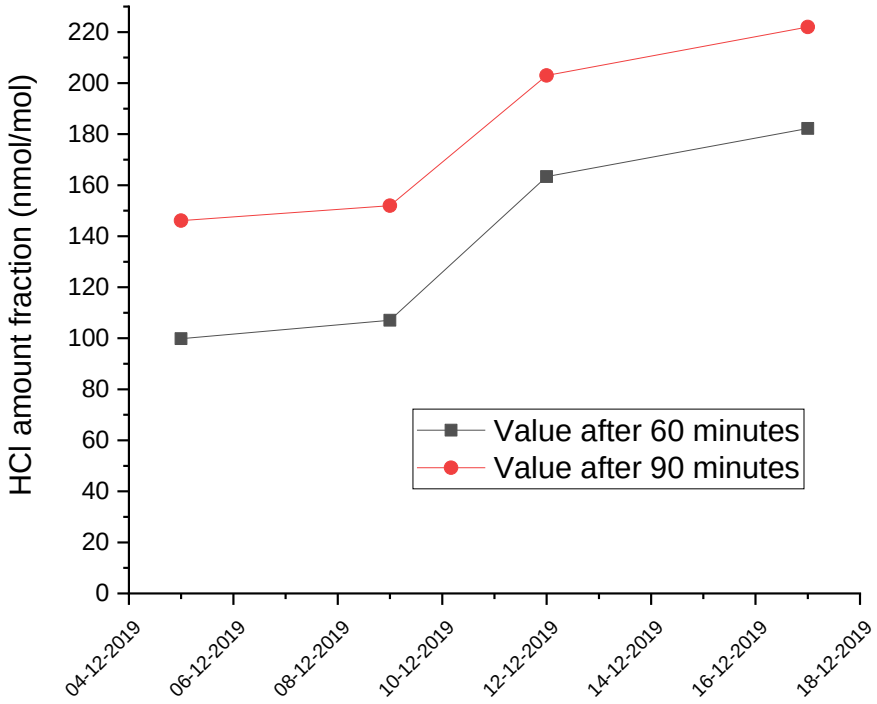

Figure 5: Short-term stability study of HCl in an Aculife IV cylinder (prepared on 29 December 2019) with a gravimetric HCl amount fraction of 399 ppb (VSL526712) – Test 1

Figure 5 shows the measurement results for HCl at a nominal 400 ppb amount fraction. Measurements of the two 100 ppb HCl mixtures were started but abandoned after 2 days as (almost no HCl was detected. The analysis shows that the very long measurements are needed in order for the HCl to get out of the cylinder even through only coated materials (liner, pressure regulator and tubings) were used. It is hypothesized that the cylinder valve plays an import role in this.

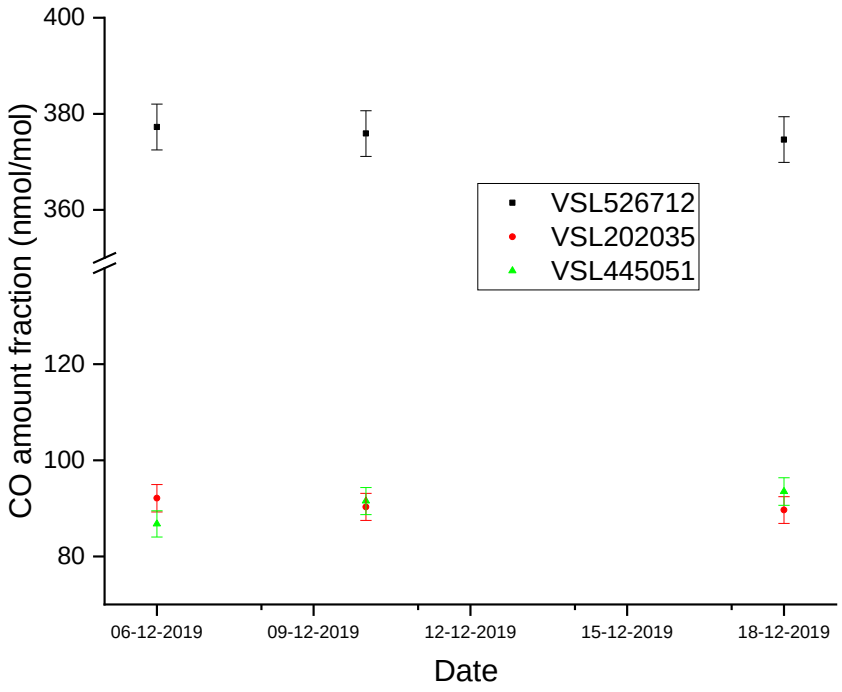

Figure 6: Results of the short-term stability of CO at 100 and 400 ppb (the mixture also containing HCl)

For CO, all values indicate some initial within sampling vessel upon collection (VSL 526712: 403 ppb, VSL 202035: 106 ppb, VSL445051: 104 ppb) yet the stability is good for the 3 mixtures.

4 - Preparation of the cylinders before sampling

In order to sample a volume of hydrogen that is fully representative of the fuel dispensed at the station, every step from the vessel preparation to the transportation must be undertaken following procedures that have been validated.

To avoid false positives from air and moisture contamination, a rigorous evacuation or purging cycle must be performed. There is currently no standard procedure for the preparation of sample cylinders for hydrogen fuel quality control even if purging procedures are mentioned in ASTM D7606-11 [3] and ISO19880-1 [2].

Relevant and validated preparation methods are presented in the MetroHyVe report 4.1.7 “Good practice guide on effective sampling and transportation of hydrogen from the refuelling station as required by ISO14687” [9] so these methods will not be described here. This practice guide presents two evacuation procedures to prepare cylinders before sampling; a method using purging cycles and a method using turbo evacuation.

Moreover, in the guide, a method to pre-fill the cylinder with UHP hydrogen is also presented. This method presents two advantages: 1) air and moisture ingress into the cylinders is minimised as it is more likely that hydrogen from the cylinder would egress; consequently pre-filled cylinders can be

stored safely for a longer period than evacuated sampling cylinders and 2) the hydrogen in the cylinder is used to remove residual air present within the dead volume between the sampling apparatus and the sampling cylinder. However, preferably, the time between pre-filling the sampling vessel and taking the sample must be as short as possible.

5 - Transportation

The transport conditions must guarantee the integrity of the samples. From completion of sample collection to laboratory analysis, every effort should be made to:

- Avoid contamination of the sample with for example air and water

- Minimise any changes of the sample composition by adsorption of impurities actually present in the hydrogen onto the surfaces of the vessels.

To maintain the integrity of the samples, procedures for collection, transport, storage conditions, and security, should be designed.

As the cylinders contain hydrogen under pressure, it is unlikely that ingress of oxygen and nitrogen into the hydrogen sample would occur during the transportation time. In this aspect, filled cylinders can be stored safely for a longer period than evacuated sampling cylinders without risk of contamination. However, due to the fact that some of the species are reactive, the risk of losing impurities by adsorption to the vessels walls needs to be limited by optimising the transportation time. For this, it is preferable to prepare the transportation in advance.

Regulations related to the use, inspection and transport of cylinders are described in the MetroHyVe report 4.1.7 “Good practice guide on effective sampling and transportation of hydrogen from the refuelling station as required by ISO14687” so these regulations will not be described here.

The container shall also be appropriately marked in accordance with the regulations in force which are described in the good practice guide mentioned above.

6 – Other types of vessels: Sorbent tubes

Sorbent tubes are typically small tubes (10 cm long) made of glass or stainless steel (with or without treatment) and contain various types of solid adsorbent material. Commonly used sorbents include activated charcoal, silica gel, and organic porous polymers such as Tenax and XAD resins. Solid sorbents present the advantage to trap and retain the compound(s) of interest but not the matrix. This leads to an enrichment of the targeted compounds, which can be desorbed by heating, or extracted with solvents, for analysis. The advantage of using sorbent tubes is that they are relatively simple to use, store and transport to the laboratory.

Results obtained during MetroHyVe showed that a method based on thermal desorption—gas chromatography–mass spectrometry is promising for total species even though not all of the compounds belonging to the three “total species” listed in ISO 14687 can be quantitatively retained on one unique sorbent. This technique will not only provide a sum of concentrations but also an identification of which compound(s) is/are actually present in the hydrogen. The most suitable sorbent appears to be TCC, a three-bed sorbent, containing a weak (Tenax TA), a medium (Carbograph 1TD) and a strong sorbent (Carboxen 1003) [10]. It may, however, be necessary to sample different volumes on several tubes. Low sampling volumes reduce the risk of volatile components breaking through the

sorbent bed during sampling, but the enrichment may not be enough to reach the limit of detection required in ISO 14687, especially for sulphur compounds. A combination of small (less than 100 mL) and larger (more than 500 mL) sample volumes overcomes these issues.
Additionally, this study shows that compounds retained on the sorbent materials can be analysed several days after sampling without significant alteration of their concentration.
However, 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. Future works on implementing sampling on sorbent tubes at a HRS is necessary.

However, two possibilities for this implementation are presented in the MetroHyVe report A4.3.8 "Sampling using sorbent tubes directly at the HRS – Assessment of the feasibility" [11]

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 for the sampling on tubes.

Until then, 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 – Conclusions

In order to sample a volume of hydrogen that is fully representative of the fuel dispensed at the station, every step from the vessel preparation to the transportation must be undertaken following procedures that have been validated. The MetroHyVe project (task 4.4) has demonstrated that to avoid false positives for air and moisture a rigorous evacuation or purging cycle must be performed.

To avoid false negatives, the choice of the cylinder material and treatment is crucial. Among the characteristics for the hydrogen specifications, 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. sulfur compounds, water).

Therefore, in order to correctly assess the purity of the hydrogen dispensed at the HRS, it must be ensured that adequate sampling vessels are used. Losses occurring while the sample of hydrogen is collected at the HRS and transported to the laboratory would lead to falsely lower levels of impurities being measured than are present in the original hydrogen.

The most common materials used today for cylinders are aluminium, steel, alloys and composite materials. Even if there are a multitude of cylinders (materials, size, configuration…) and a multitude of different methods used to passivate the internal surface of cylinders, MetroHyVe project (task 4.4) has shown that not enough information is currently available to make the proper choice of sampling vessels. It lacks conclusive results from short-term stabilities performed in the conditions inherent to hydrogen purity (in term of adequate pressure, matrix, adequate concentrations, presence of several species at the same time).

The short-term stability studies performed in this project clearly demonstrate that the decision to use one cylinder should be made based on tests showing that this particular cylinder is suitable for its intended purpose, i.e. that the species to be analysed if present in the gas at concentrations below their threshold values in the hydrogen quality standards and higher, remains stable from the time of the sampling to the time of the analysis. Stability tests with several species present in the same mixture also need to be performed to conclude on possible interactions.

Stability issues were clearly observed for HCl and H_2S. CO was found to be stable in all types of vessels tested in these stability studies. However, when CO and HCl were both present in a hydrogen gas mixture, some initial losses were observed (Test 1).

The short-term stability studies for H_2S were performed at concentration 10 times higher than the ISO threshold. Even at this level, some initial losses were observed (Test 2). It can be anticipated that greater losses could be expected at even lower amount fractions (closer to the threshold). Moreover, an almost total loss of H_2S was observed when filling a Dursan treated stainless-steel cylinder. The results obtained for HCl also clearly demonstrate that there is a need for more studies of cylinders materials and treatment.

Risks for adsorption onto the sampling devices should also be assessed.

8 - References

[1] ISO14687: 2019, Hydrogen fuel quality – Product specification

[2] ISO19880-1, annex I; sampling procedures and hardware for hydrogen fuel quality analysis which is under revision in working group 24 of the technical Committee TC 197 (Hydrogen Technologies)

[3] ASTM D7606:1, Standard Practice for Sampling of High-Pressure hydrogen and related fuel cell feed gases

[4] MetroHyVe report A4.4.1 “Literature review – stet-of-art for the storage of reactive species in vessels”, www.metrohyve.eu

[5] MetroHyVe report A4.1.2 “Recommendations regarding the conditions for sampling at the HRS”, www.metrohyve.eu

[6] “The performax cylinder passivation: a brand new approach for aluminium cylinders, G. Squire,, effecTech, Gas Analysis conference 2017, D.09

[7] “The use of coatings to improve the physical and analytical reliability of process monitors used for ammonia, Mercury and hydrogen sulfide service”, SilcoTek notes, G. Barone, M. Higgins, D.Smith

[8] Dursan® and SilcoNert® 2000 Coating Comparison Guide, https://www.silcotek.com/hs-fs/hub/22765/file-527701750-pdf/docs/Dursan_Material_Comparison.pdf

[9] MetroHyVe report 4.1.7 “Good practice guide on effective sampling and transportation of hydrogen from the refuelling station as required by ISO14687”, www.metrohyve.eu

[10] Hydrogen Purity Analysis: Suitability of Sorbent Tubes for Trapping Hydrocarbons, Halogenated Hydrocarbons and Sulphur Compounds , K. Arrhenius, H. Bohlen, O. Büker, I. de Krom, D. Heikens,J. van Wijk, *Appl. Sci.* 2020, *10*(1), 120; https://doi.org/10.3390/app10010120

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