METROLOGY for HYDROGEN VEHICLES 2

Deliverable D5

Good practice guide for handling of hydrogen fuel sampling containers (harmonised with USA and Japan and including preparation, delay for analysis, lifetime and transfer) at HRS nozzles

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Summary

This good practice guide was written as part of activity 3.1.9 from the EMPIR Metrology for Hydrogen Vehicles 2 (MetroHyVe2) project. The three-year European project commenced on 1st August 2020 and focused on providing solutions to four measurement challenges faced by the hydrogen industry (flow metering, quality assurance, quality control, sampling and fuel cell stack testing). For more details about this project please visit https://www.sintef.no/projectweb/metrohyve-2/.

Confidentiality	Public

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1. Introduction

Hydrogen fuel quality is important for the deployment of hydrogen solutions in Europe. The international standards require the measurement of 14 compounds including reactive compounds at challenging levels (e.g., nmol/mol) as shown in Table 1. Challenges to ensure hydrogen fuel quality are related to the measurement complexity of the compounds in ISO 14687 [1] or EN 17124 [2]. The measurements at these levels are challenging and often require instrumentation only available in an analytical laboratory (and not currently possible with online analysers or sensors). Moreover, the complexity of the refuelling process, filling process, temperature, pressure, and the requirement for the nozzle sampling/measurement makes it really challenging for online analysis at the nozzle.

Table 1. List of compounds and amount fraction specified in the international standard ISO 14687 [1] and EN 17124 [2]

Component	ISO 14687 /EN 17124 threshold amount fractions (µmol/mol)
Nitrogen	300
Helium	300
Argon	300
Carbon monoxide	0.2
Carbon dioxide	2
Methane	100
Non methane hydrocarbons	2 (methane equivalent)
Oxygen	5
Water	5
Ammonia	0.1
Formaldehyde	0.2
Formic acid	0.2
tot halogenated	0.05
tot sulphur	0.004

Therefore, hydrogen purity testing is realised by hydrogen samples collected in gas cylinders which are then sent to testing laboratories for analysis. The gas containers are extremely important to ensure that the results are accurate and representative. For example, the cylinder could take several weeks to reach the testing laboratory depending on how far it must travel. To ensure representative sampling, the sampling cylinder must be able to retain contaminants at the challenging amount fractions specified in the standard EN 17124 for at least few months.

A lot of the contaminants specified by the EN 17124 are reactive, such as ammonia, formic acid, formaldehyde, halogenated compounds, and the sulphur compounds. They are known to interact with the surface of the gas container (i.e., adsorb, react, create by-product). Such interactions may result in a loss of the reactive compounds in the gas phase. Losses of reactive compounds during sampling or transport could cause a "false negative" (contaminants in the hydrogen fuel being are measured lower than the true value). This false negative could then mean that a hydrogen refuelling station (HRS) is supplying contaminated gas without realising it. Moreover, it would continue undetected for a certain time to provide hydrogen fuel to fuel cell electrical vehicle (FCEV) users until an issue occurred. Such undetected contamination may cause loss of performance to the customer vehicle due to the presence of the contaminant. Also, false positives are possible if compounds react to generate by-products. A false positive will result in an overestimation of the real amount fraction of the compounds. For example, oxygen react with hydrogen to become water, then water amount fraction will increase compared to its real level in the hydrogen fuel (false positive) while oxygen amount fraction will reduce compared to its real level (false negative). It may cause the hydrogen fuel to be considered non-compliant while it is just an analysis realised too long after the sampling or in an improper container.

To be suitable for sampling, a gas cylinders or container shall have no initial amount fraction loss of the analytes of interest and be able to keep the analytes stable within uncertainty in the cylinder for an adequate amount of time to allow transport. The knowledge of gas cylinder (including its passivation) performance for hydrogen fuel contaminants (e.g., EN 17124) is critical to determine its suitability for sampling. The selection of a suitable cylinder would ensure representative results are provided to the HRSs and allow good performance of the FCEV. Beside selecting the suitable cylinder is critical, the lifetime or history of the cylinders needs to be understood too. The impact of the age of the internal treatment and repetitive samplings may impact the performance of the gas cylinder and need to be understood. Such impact may reduce the lifetime of a gas cylinder for this specific application if the degradation of the internal passivation of a cylinder lead to degraded performance (i.e., no longer able to retain a reactive compounds).

In this good practice guide, a summary of the current state of the art is provided and then updated with the recent studies of MetroHyVe 2 on cylinder suitability. The impact of repetitive samplings and cylinder aging will be discussed based on recent MetroHyVe 2 studies.

2. Previous studies and current state of the art

A large selection of cylinder internal passivation treatments is currently available (i.e., Sulfinert®, Aculife VII, Performax, SPECTRA-SEAL). As part of MetroHyVe 2 consortium, K. Arrhenius et al [3] realised a peer review of the stability tests for compounds specified in the ISO 14687 in gas containers. The summary table is presented below.

Table 2. *Summary of cylinder suitability for a period of 4 months from K. Arrhenuis et. al [3].*

Compounds	Stainless steel				aluminium									
	Untreated		Sulfinert®		Untreated		Aculife VII		Performax		SPECTRA-SEAL		Untreated SGS	
	a	b	a	b	a	b	a	b	a	b	a	b	a	b
C_2H_6	X	X	X	X	X	X	X	X	X	X	S	S	S	S
He	X	X	X	X	X	X	X	X	X	X	S	S	S	S
N_2	X	X	X	X	X	X	X	X	X	X	S	S	S	S
Ar	X	X	X	X	X	X	X	X	X	X	S	S	S	S
CO_2	X	X	X	X	X	X	X	X	X	X	S	S	S	S
CO	i.d.	S	i.d.	S	S	S	i.d.	i.d.	i.d.	i.d.	S	S	S	S
H_2S	i.d.	I/S	X.	S	i.d.	I	i.d.	I	i.d.	i.d.	I	I	S	i.d.
HCl	i.d.	i.d.	i.d.	I	i.d.	i.d.	i.d.	I	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.
CH_2O	i.d.	i.d.	i.d.	S∗	i.d.	i.d.	i.d.	i.d.	i.d.	S∗	I	I	I	i.d.
CH_2OH	i.d.	i.d.	i.d.	i.d.	i.d.	X.	i.d.	i.d.	i.d.	i.d.	S	S	I	i.d.
NH_3	i.d.	i.d.	i.d.	X	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	I	X	I	i.d.
O_2	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	S^c	S^c	S^c	S^c
H_2O	i.d.	i.d.	X^d	X^d	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	S^d	S^d	S^d	S^d

a: at ISO14687:2019 threshold.
b: at Higher concentrations (i.e., 50 times ISO 14687).
X: should be suitable.
S: suitability demonstrated (∗ more than 80% stability over at least a month).
I: Issues were found (ex. of issues: need careful selection of the cylinder, initial loss …).
i.d.: Insufficient data.
[c] Oxygen stability seems to vary between cylinders of same internal treatment.
[d] Oxygen reactivity may affect the amount fraction of water through the reaction in hydrogen matrix.

It was noted by Arrhenius et al. that very few tests have been conducted in hydrogen matrix [3]. A lot of the more challenging compounds such as formic acid, ammonia and formaldehyde had insufficient data in the different cylinder types.

The objective of MetroHyVe 2 study was, therefore, to focus on gathering more data on these more challenging compounds in all the known cylinders used for hydrogen sampling in 2021. Another MetroHyVe 2 activity (A2.2 stability studies for reference materials) was used to provide further information where stability is expected but was not currently evidenced in the literature. All these new data were used to update the current state of the art review from Arrhenius et al. [3] and support better selection of suitable cylinder for hydrogen fuel quality

3. Results from MetroHyVe 2 sampling cylinder stability testing

3.1. Terminology and definition

Several terms need to be defined to better understand the actual suitability of cylinder for hydrogen fuel sampling. The definitions were proposed by MetroHyVe 2 team and used in the report.

Table 3. *List of definition around cylinder suitability and stability for hydrogen fuel quality*

Suitable cylinder	a suitable cylinder is a cylinder that allows the compounds to be stable for a 4-month period within a reasonable uncertainty and did not show any initial loss. It is a combination of stability and no initial loss.
Stability	a stable cylinder is a cylinder that had a consistent measured value of the contaminant of interest over the 4-month period within a reasonable uncertainty.
Initial loss/increase	an initial loss or increase is a significant difference in the amount fraction on first measurement compared to the gravimetric amount fraction that should be present in the cylinder (e.g., by adsorption to the cylinder walls).
Unsuitable	a cylinder that is deemed unsuitable for use for hydrogen sampling is a cylinder has an initial change in amount fraction that could lead to false positives or negatives and/or is unable to keep the component of interest stable for a 4-month time.

3.2. Stability studies of reactive compounds in hydrogen in gas cylinders

3.2.1. New results for reactive compounds

As part of the MetroHyVe2 project, a large selection of different types of cylinders were tested for stability of reactive compounds to gather more data on which cylinders would be suitable for collecting samples. The cylinders were chosen to reflect current sampling practices in 2021 around the world (stainless steel Sulfinert® for US sampling, manganese steel for Japan sampling, SPECTRA-SEAL for Europe sampling) but also to investigate potential of new cylinder passivation that could be suitable for hydrogen fuel sampling.

The cylinders tested were 10L aluminium SPECTRA-SEAL (BOC, UK), 10L aluminium SGS internal surface finish (Luxfer, UK), 10L aluminium DB Gold (EffecTech, UK), 10L aluminium Aculife III (Air Liquide, France), 5L aluminium AlphaTech (Air liquid, France), 5L aluminium H2 Mobility (Air Liquide, France), 30L aluminium White Tope (Air Liquide, US), 47L manganese steel (Benkan Kikoh, Japan), 10L atomic layer disposition (ALD) coated steel (Linde, Germany) and 2.25L stainless steel Sulfinert® (Restek, US).

The study objective was to test the stability of more reactive compounds and collect data on contaminants listed in the EN 17124 standard that do not have much data currently in the literature. Therefore, the following components were selected by the partners to be studied: formic acid, formaldehyde, ammonia, hydrogen sulphide and hydrogen chloride. The amount fractions selected for the reactive contaminants were around double the limit specified by EN 17124. The exception being ammonia which was decided to test at four times the EN 17124 specified limit to allow data of stability to be collected even in the event of initial losses that have been seen previously.

Results from the Activity 2.2 in the MetroHyVe 2 project identified that the formaldehyde and formic acid seemed to react with ammonia in hydrogen matrix. The study of the stability was, therefore, split into a separate set of mixtures: set 1 with ammonia only and set 2 with formaldehyde, formic acid, hydrogen sulphide and hydrogen chloride. This was done to allow data to be gathered on the stability of the components without loss due to their reaction. The study length was set at 4 months. The stability study length was considered sufficient to simulate lengthy transport of cylinders.

The analytes of interest (ammonia, formic acid, hydrogen chloride etc) all had possible interactions with water. If there was any difference in stability behaviour of these reactive compounds with water presence this could affect samples as water is a contaminant that has a high likelihood of occurrence. The targeted compounds stability in hydrogen matrix were tested without and with the presence of water.

The detailed preparation of the different mixtures studied can be found in Annex A.

3.2.1.1. Results for stability of reactive compounds in hydrogen fuel without water

The results of the stability studies conducted in MetroHyVe 2 are summarised in Table 4 and Annex B.

Table 4. *Summary of results from stability studies of reactive compounds without water in different types of cylinders. The colour coding means green: suitable; yellow: suitable under limited conditions; red: unsuitable*

	Steel			Aluminium						
Compounds	**Stainless steel Sulfinert®**	**Manganese steel**	**ALD-Coated steel**	**SPECTRA-SEAL**	**SGS**	**AlphaTech**	**H2 Mobility**	**white top**	**Aculife III**	**DB Gold**
Formic acid	Suit	Uns, IL-Stab	Uns, IL	Suit	Uns, IL-Stab	Uns, IL	Uns, IL-stab	Uns, IL	Uns, IL	Suit
Formaldehyde	Suit	Uns, Stab* (2 weeks)	Uns, Stab** (1.5 months)	Suit	Suit	Suit	Suit	Suit	Suit	Suit
Hydrogen sulphide	Uns, Stab** (1.5 months)	Uns, Stab* (1 week)	Uns, IL	Uns, IL-Stab	Uns, Stab** (1.5 months)	Uns, IL-Stab	Uns, IL-Stab	Uns, Stab** (1.5 months)	Uns, IL-Stab	Suit†
Hydrogen chloride	Uns, IL-Stab	Uns, IL-Stab	Uns, IL-Stab	Suit	Uns, IL-Stab	Uns, IL-Stab	Uns, IL-Stab	Uns, IL	Uns, IL-Stab	Suit
Ammonia	Suit	Uns, IL-Stab	Uns, IL-Stab	Uns, IL	Uns, IL	Uns, IL-Stab	Suit	Uns, IL	Suit	Suit

Suit	Stable to gravimetric amount fraction within 95% confidence level for duration of the study (4 months)
†	Additional sulphur containing components were present in the gas cylinder
Uns	Unsuitable for sampling this compound at EN 17124 amount fraction
IL	Unsuitability due to an initial loss of the compound compared to gravimetric value
Stab	Unsuitability due to compound instability in the cylinder for the duration of the study
*	Unstable but suitable for very short time (1-2 week), stability uncertainty including decay is similar to stable cylinders for this period. The stability period is provided in brackets, only useful for very short transport
**	Unstable but suitable for short time (1-2 month), stability uncertainty including decay is similar to stable cylinders for this period. The stability period is provided in brackets, only useful for short transport

The results in the table show the difficulties in finding gas cylinders that are suitable for all the reactive components at close to the ISO 14687 threshold levels. Most cylinders are suitable for some but not all the contaminants tested. Only the recent DB Gold cylinder showed good performance for all compounds tested. It highlights the need for more research into cylinder passivation techniques and treatment.

3.2.1.2. Impact of water on cylinder performance and suitability

The results of the stability study with or without water showed variation in the stability of studied compounds (see Annex B). The effect of water presence was an increase in the stability of the compounds present. Formaldehyde showed improved stability in the manganese cylinder when 5 µmol/mol water was present. Water is used as a stabilising agent for formaldehyde, so it is possible that the water is improving the stability of formaldehyde amount fraction within the cylinder. Additionally, the formic acid in ALD-coated steel, the SGS, the White Top and the Aculife III cylinders showed better stability in the mixtures where water was present, which was different to the behaviour seen in the mixtures without water. The Sulfinert®, SGS and White Top cylinders also showed improved stability for hydrogen sulphide when water was present, remaining stable for the whole 4 month period of the study rather than only the 1.5 month period when water was not present. Since the presence of water has a stabilising effect, the Table 4 summarises the stability of the studies without water as these were the conditions with the shorter stability period.

3.2.2. Impact of valve treatment on cylinder performance and stability

The cylinder and valve cylinder may come from different suppliers and may be of different material (e.g., aluminium cylinder and stainless-steel valve) [4]. Therefore, the valves may have a different treatment or passivation as the cylinder. The impact of valve passivation was studied in this report.

In each batch of study cylinders, two SGS aluminium cylinders were used, one which had a Sulfinert® treated stainless steel valve and one which had an untreated stainless-steel valve. This was done to investigate if using a treated valve had any effect on stability of the components in the cylinder. The results for the stability of the SGS cylinder with the treated and non-treated valve can be found below in Table 5 and in Annex B.

Table 5. *Summary of results of stability of reactive compounds without water for cylinders of SGS finished fitted with treated and non-treated stainless-steel valves. The colour coding means green: suitable; yellow: suitable under limited conditions; red: unsuitable.*

	Aluminium SGS finish	
Compounds	**Stainless steel valve with Sulfinert® treatment**	**Stainless steel valve without any treatment**
Formic acid	Uns, IL-Stab	Uns, IL-Stab
Formaldehyde	Suit	Suit
Hydrogen sulphide	Suit	Uns, Stab** (1.5 months)
Hydrogen chloride	Uns, IL, stab	Uns, IL-Stab
Ammonia	Uns, IL	Uns, IL

Suit — Stable to gravimetric amount fraction within 95% confidence level for duration of the study (4 months)
Uns — Unsuitable for sampling this compound at EN 17124 amount fraction
IL — Unsuitability due to an initial loss of the compound compared to gravimetric value
Stab — Unsuitability due to compound instability in the cylinder for the duration of the study
** — Unstable but suitable for short time (1-2 month), stability uncertainty including decay is similar to stable cylinders for this period. The stability period is provided in brackets, only useful for short transport

For formic acid, formaldehyde, ammonia, and hydrogen chloride, no significant difference was seen on the stability of the contaminants with the different valve types. It was concluded that the cylinder internal treatment had a much larger influence on stability of these contaminants than the treatment of the valve present on the cylinder. For hydrogen sulphide better stability was seen for the cylinder with the treated valve. A stability of 1.5 months was observed for the SGS cylinder with the untreated valve, and a stability of 4 months was seen for the SGS cylinder with the treated valve. The summary of results in Table 3 shows the summary of results for the SGS cylinders without treated valves as these would be considered 'normal' conditions. However, the study demonstrated that using a passivated valve may improve the cylinder performance.

3.3. Cylinder lifetime impact on performance (aged and used cylinders)

The sampling cylinders being used to collect the hydrogen fuel samples may have a long lifetime. Cylinders are required to be pressure tested every 10 years and some treatments have a specified lifetime (for example SPECTRA-SEAL are guaranteed for 5 years after application to the cylinder). It is important to understand how the history of a gas container (e.g., multiple samplings, age of the internal treatment of the cylinder) will affect the performance of the cylinder and therefore the stability of the contaminant in the hydrogen fuel sample. The composition tested in the cylinder was formaldehyde, formic acid, hydrogen sulphide, water and hydrogen chloride as shown in Annex A.

The results of aged and multiple sampling SPECTRA-SEAL cylinder (Table 5) showed a decrease in performance in all cases. The results were coherent with the supplier information about the passivation lifetime. For the multiple sampling results, it should be considered that the cylinder went over the 5 years lifetime during the testing. The number of samplings didn't significantly change the results compare to the aged cylinder.

Table 6. *Summary of stability studies on old cylinders and cylinders that had been used for multiple samplings for aluminium SPECTRA-SEAL cylinders. The colour coding means green: suitable; yellow: suitable under limited conditions; red: unsuitable.*

	Aluminium SPECTRA-SEAL				
Compound	**Aged cylinder 1**	**Aged cylinder 2**	**Used cylinder 1**	**Used cylinder 2**	**New cylinder**
Cylinder age and sampling number	6 year 0 sampling	6 year 0 sampling	5.5 year 3 samplings	5.5 year 3 samplings	2.2 years 0 sampling
Formic acid	Uns, Stab** (2 months)	Uns, Stab* (2 weeks)	Uns, Stab** (2 months)	Uns, Stab* (2 weeks)	Suit
Formaldehyde	Suit	Suit	Suit	Uns, Stab** (1.5 month)	Suit
Hydrogen sulphide	Uns, IL	Uns, IL	Uns, IL	Uns, IL	Uns, IL Stab
Hydrogen chloride	Uns, IL	Uns, IL	Uns, IL	Uns, IL	Suit

Suit Stable to gravimetric amount fraction within 95% confidence level for duration of the study (4 months)
Uns Unsuitable for sampling this compound at EN 17124 amount fraction
IL Unsuitability due to an initial loss of the compound compared to gravimetric value
Stab Unsuitability due to compound instability in the cylinder for the duration of the study
* Unstable but suitable for very short time (1-2 week), stability uncertainty including decay is similar to stable cylinders for this period. The stability period is provided in brackets, only useful for very short transport
** Unstable but suitable for short time (1-2 month), stability uncertainty including decay is similar to stable cylinders for this period. The stability period is provided in brackets, only useful for short transport

Table 7. *Summary of stability studies on old vs new stainless steel Sulfinert® treated cylinders. The colour coding means green: suitable; yellow: suitable under limited conditions; red: unsuitable.*

	Stainless steel Sulfinert®	
Compound	**Aged cylinder**	**New cylinder**
Cylinder age and sampling number	6 years 0 sampling	4 years 0 sampling
Formic acid	Uns, IL	Suit
Formaldehyde	Uns, IL	Suit
Hydrogen sulphide	Uns, IL	Uns, Stab** (1.5 months)
Hydrogen chloride	Uns, IL	Uns, IL-Stab

Suit Stable to gravimetric amount fraction within 95% confidence level for duration of the study (4 months)
Uns Unsuitable for sampling this compound at EN 17124 amount fraction
IL Unsuitability due to an initial loss of the compound compared to gravimetric value
Stab Unsuitability due to compound instability in the cylinder for the duration of the study
** Unstable but suitable for short time (1-2 month), stability uncertainty including decay is similar to stable cylinders for this period. The stability period is provided in brackets, only useful for short transport

The results of Stainless steel Sulfinert® cylinder (Table 6) shows a particularly large difference in stability to the new cylinder with loss of all components when previously stability was shown for formic acid and formaldehyde.

These results imply that aging and re-use of a cylinder can influence the stability of the components sampled and degradation of performance. Further investigation should, therefore, be undertaken to investigate how long it takes or how many samplings may affect the stability of contaminants in the different types of cylinder treatments deemed suitable for sampling.

4. Recommendation and good practice on cylinder suitability for hydrogen fuel sampling

The studies realised in MetroHyVe 2 project provides new evidence and good practice to select, use and manage cylinders for hydrogen samplings.

4.1. Updated state-of-the-art of cylinder suitability

The MetroHyVe 2 studies present a significant update to the current state of the art in term of cylinders tested, open data, stability results that are available for each cylinder and compounds. Detailed results are provided in Annex B.

The result from the MetroHyVe 2 stability studies (WP2 and WP3) have been used to update the state-of-the-art review from K. Arrhenius et al. [3]. The Table 8 present the new updated state of the art on cylinder suitability for hydrogen fuel sampling. It can be the basis for the selection of the most suitable cylinder for hydrogen sampling based on the compounds targeted.

The study highlighted some issues related to compounds behaviour in gas phase. It should be noted that cross reactivity can't be considered in such cylinder suitability table. For example, formaldehyde and formic acid stability were affected by the presence of ammonia and vice versa. As these compounds are reacting together, the presence of ammonia and formic acid or formaldehyde would result in loss of both compounds. However, such effect is not due to the gas cylinder and therefore can't be considered as a source of instability. It may highlight the need for further guidance by the industry on compounds relevance in hydrogen fuel.

The MetroHyVe 2 study presented results from one cylinder of each type. The production of cylinder is realised by batch, the impact of the production process and suitability of each batch is currently unknown. It is critical to ensure that cylinder's performance is homogenous within batch and between batches. This aspect wasn't studied by MetroHyVe 2 partners, but it is a relevant next step to ensure that performance from gas cylinder manufacturer is consistent over time and with the results of the cylinders studied. It has been reported that oxygen stability varied within and between batches of gas cylinder, producing water, leading to the footnotes in the Table from Arrhenius et al. review [3] on the stability of the oxygen and water.

Table 8. *Summary of results from the MetroHyVe 2 WP2 and WP3 results for contaminants at amount fractions close to or at the ISO 14687 threshold values. The table was based and updated from Arrhenius et al. [3]. The colour coding means green: suitable; yellow: suitable under limited conditions; red: unsuitable. Total sulphur has been assessed by taking the conservative approach. If one of the two sulphur compounds tested showed unsuitability, therefore the overall cylinder was considered unsuitable.*

	Steel				Aluminium								
Component	**Stainless steel Sulfinert®**	**Manganese steel**	**ALD-Coated steel**	**Untreated stainless steel**	**SPECTRA-SEAL**	**Untreated SGS**	**H2 Mobility**	**Aculife VIII**	**Aculife III**	**White top**	**AlphaTech**	**Performax**	**DB Gold**
He	Suit	X	X	X	Suit	Suit	Suit	X	X	Suit	X	X	Suit
N_2	Suit	Suit	Suit	X	Suit	Suit	Suit	X	Suit	Suit	Suit	X	Suit
Ar	Suit	X	X	X	Suit	Suit	Suit	X	X	Suit	X	X	Suit
CO_2	Suit	X	X	X	Suit	Suit	Suit	X	X	Suit	X	X	Suit
CO	Suit	i.d.	i.d.	i.d.	Suit	Suit	Suit	i.d.	i.d	Suit	i.d.	i.d.	Suit
Tot S	Uns, Stab**	Uns, Stab*	Uns, IL	i.d.	Uns, IL-stab	Uns, Stab **	Uns, IL- stab	i.d.	Uns, IL-stab	Uns, Stab**	Uns, IL-stab		Uns,stab†
H_2S	Uns, Stab**	Uns, Stab*	Uns, IL	i.d.	Uns, IL-stab	Uns, Stab **	Uns, IL- stab	i.d.	Uns, IL-stab	Uns, Stab**	Uns, IL-stab	i.d.	Suit†
OCS	Suit	i.d.	i.d.	i.d.	Suit	Suit	Suit	i.d.	i.d.	Suit	i.d.	i.d.	Uns,stab
HCl	Uns, IL-Stab	Uns, IL-stab	Uns, IL-stab	i.d.	Suit	Uns, IL- stab	Uns, IL- stab	i.d.	Uns, IL-stab	Uns, IL	Uns, IL-stab	i.d.	Suit
CCl_2H_2	Suit	i.d.	i.d.	i.d.	Suit	Suit	Suit	i.d.	i.d.	Suit	i.d.	i.d.	Suit
CH_2O	Suit	Uns, Stab*	Uns, Stab**	i.d.	Suit	Suit	Suit	i.d.	Suit	Suit	Suit	i.d.	Suit
CH_2OH	Suit	Uns, IL-Stab	Uns IL	i.d.	Suit	Uns, IL- stab	Uns, IL-stab	i.d.	Uns, IL	Uns, IL	Uns, IL	i.d.	Suit
NH_3	Suit	Uns, IL-Stab	Uns, stab	i.d.	Uns, IL	Uns, IL	Suit	i.d.	Suit	Uns, IL	Uns, IL-stab	i.d.	Suit
O_2	Suit	i.d.	i.d.	i.d.	Suit	Suit	Suit	i.d.	i.d.	Suit	i.d.	i.d.	Suit
H_2O	Suit	i.d.	i.d.	i.d.	Suit	Suit	Suit	i.d.	i.d.	Suit	i.d.	i.d.	Suit
C_3H_8	i.d.	i.d.	i.d.	i.d.	Suit	Suit	Suit	i.d.	i.d.	Suit	i.d.	i.d.	Suit
CH_4	Suit	X	X	X	Suit	Suit	Suit	i.d.	X	Suit	X	X	Suit
C_2H_6	Suit	X	X	X	Suit	Suit	Suit	X	X	Suit	X	X	Suit

X	should be suitable (no published data available)
i.d.	insufficient data
†	Additional sulphur containing components were present in the gas cylinder
Suit	Stable to gravimetric amount fraction within 95% confidence level for duration of the study (4 months)
Uns	Unsuitable for sampling this compound at EN 17124 amount fraction
IL	Unsuitability due to an initial loss of the compound compared to gravimetric value
Stab	Unsuitability due to compound instability in the cylinder for the duration of the study
*	Unstable but suitable for very short time (1-2 week), stability uncertainty including decay is similar to stable cylinders for this period. The stability period is provided in brackets, only useful for very short transport
**	Unstable but suitable for short time (1-2 month), stability uncertainty including decay is similar to stable cylinders for this period. The stability period is provided in brackets, only useful for short transport

https://www.sintef.no/projectweb/metrohyve-2

4.2. Sampling cylinder selection for hydrogen sampling

Based on Table 7, the Sulfinert® stainless steel and DB Gold cylinders showed the best stability for most compounds. These cylinder types were the most suitable cylinder for sampling hydrogen fuel. However, there is still some issues using this cylinder alone. The DB Gold cylinder showed an increase in total sulphur amount fraction over time, whereas the Sulfinert® Stainless steel showed short stability of 1.5 month for total sulphur amount fraction and would provide false negative for HCl amount fraction (initial loss). Several of the cylinders (H2 Mobility, SPECTRA-SEAL, SGS) showed suitability or at least 1.5-month stability for more than 75 % of the compounds tested. The components that were unstable also varied between these cylinders. Hydrogen fuel sampling would require multiple samplings of the same HRS into different cylinders to have the potential to have representative results for all the reactive compounds across the samples taken. A mitigation may be considered based on the probability of contaminant presence related to ISO 19880-8 [5] which may allow hydrogen fuel sampling into one cylinder. Such mitigation needs to be clearly detailed and documented by the HRS owner.

The Sulfinert® treated valve on the SGS cylinder increased the stability period of the hydrogen sulphide form 1.5 months to 4 months but had no significant effect on the stability of formic acid, formaldehyde or HCl. It is expected that Sulfinert® valve will not improve the suitability for inert compounds. Therefore, the use of Sulfinert® treated valve seems to improve stability for sulphur compounds. It can be implemented for cylinder showing insufficient stability for sulphur compounds (e.g., SPECTRA-SEAL, Untreated SGS, H2 Mobility, ALD-Coated steel or manganese steel) but would require study to determine the new stability period.

The presence of water at around 5 µmol/mol (the EN 17124 threshold level) in the study didn't seem to have a detrimental effect on the stability of the reactive compounds in the cylinders tested. This means the presence of water at close to the EN 17124 threshold in samples taken would not be a cause for concern with regards to the time frame for transport and analysis of hydrogen fuel sample.

The results of the study, therefore, look promising as the cylinders studied show that sampling using one suitable or two complimentary suitable sampling vessels should allow representative sampling of the reactive compounds specified in the EN 17124 standard if a transport time of 1.5 months is achieved.

4.3. Recommendation on cylinder lifetime for hydrogen fuel application

The aging of the internal passivation of a cylinder influenced stability of very low-level reactive contaminants, most prominent in the stainless steel Sulfinert® cylinder. Only two differing cylinder passivation treatments were tested but the aged cylinders (over 5 years) did show reduced performance compared to the new cylinders present in the same study. Therefore, the lifetime of cylinder passivation types for hydrogen fuel sampling requires further investigation.

It is recommended to use the passivated cylinder within the manufacturer recommended time (e.g., 5 years for SPECTRA-SEAL cylinder). If not respected, the performance degradation observed caused significant "false negative" when reaching over 5 years. It is recommended to keep track of the age of cylinder and replace them in due time. As passivation is realised on new cylinder, information on the cylinder passivation age can be deduced from the pressure testing engraved date on the cylinder.

The repetitive sampling also seemed to influence the suitability of the cylinders. The cylinders that had had repetitive sampling showed a similar reduced performance to the aged cylinders. However, the used cylinders were 5.5 years old when used for the study and so the SPECTRA-SEAL passivation was also outside the manufacturer's guarantee period. As the suitability for one of the repetitive sampling cylinders was similar than the aged cylinders, discriminating the effect from aged to use was difficult within this study. The same recommendation not to use the cylinder past the manufacturer's guarantee of the passivation treatment would apply for multiple samplings. Further study on repetitive samplings may be required using recent cylinders (within 2 years old). Such studies would be facilitated by the increase of hydrogen fuel sampling and the increase of HRS in Europe.

4.4. Cylinder handling

Despite not being part of the MetroHyVe 2 study which focussed on the cylinder itself, the sample handling from the sample cylinder to the analytical equipment should also be considered as a possible source of variation. The handling system is defined as the pressurised equipment that will allow the transfer of the gas mixture from the cylinder outlet valve to the analyser system (e.g., pressure regulator, connector, tubing, valves, metering system). The handling system is independent of the cylinder and often proprietary of the analytical laboratory. The analyst should be careful not to confuse cylinder instability with a variation of the analyser response caused by the handling system. For example, the handling system could affect the stabilisation time of the samples being run, for example different stabilisation times for HCl standards depending on the regulator system [6]. In this case, a two identical gas mixture analysed for the same duration may show different results if the analyst uses different regulators for the handling system (e.g., sample cylinder with different valve outlet, samples with significantly different pressure). It may be challenging in term of results suitability (inaccurate results) and require understanding of the handling system, its critical parts and equivalence if modification are required and the required time to condition the system to achieve reliable result.

4.5. Good practice summary

For the hydrogen gas cylinders, the following good practice and recommendation can be followed:

- **Select a suitable cylinder** (check Table 8) or ensure the cylinder has been properly tested
    - DB Gold and Sulfinert® stainless steel were the most suitable cylinders in this study
    - New cylinder needs to be evaluated for performance in suitable conditions (close to ISO 14687 threshold)
- **Age and history of the cylinder** are critical to performance
    - Request cylinder lifetime from manufacturer
        - Without clear indication for the treatment suitability period, a 5 years period is recommended for use.
    - Ensure and monitor cylinder age and use
    - Do not use the cylinder past the manufacturer guidance except if new evidences available
    - Repetitive sampling may have an effect on the treatment of the sampling vessel. Cylinder over 5 samplings may require performance evaluation (e.g., monitoring reactive compounds over time)
- **Sample handling** ensure the handling system is suitable and validated for the compounds undergoing analysis (including the stabilisation time of the analyte). Passivated connections, regulators and tubing when analysing reactive compounds (e.g., H_2S) are recommended.

- **Passivated valve is not essential** but will improve the performance of some unsuitable cylinders for sulphur compounds.

5. Perspective

The experiments in the MetroHyVe 2 studies showed the difficulty in producing a cylinder treatment that would be able to get a representative sample of gas for all the reactive components specified in ISO 14687 within one cylinder. To get a representative sample, it may, therefore, be necessary to take samples into multiple cylinders of differing passivation treatments if a full scope analysis is required.

5.1. Research on cylinder passivation

The results also showed the difficulty in finding cylinders that can stabilise the reactive components for a least 4 months. Many cylinders were able to stabilise some of the more difficult components (such as hydrogen sulphide and formic acid) but often not all the components at the same time. This could possibly be due to interaction with other components in the cylinder but highlights the need to invest more research into new passivation and online analysis to circumvent the need for sampling for analysis of the more reactive gases.

5.2. Research on gas handling

The report highlights the low information available on the gas handling (from gas cylinder to analyser). Some information available from different studies were used to highlight its importance and how it could lead to measurement issue unrelated to the actual cylinder stability. However, it lacks dedicated study to better understand the impact of the critical parts of the gas handling (pressure regulator, pipe, valves) and the impact of passivation or treatment (e.g., Sulfinert®) on the overall results.

5.3. Cross-reaction and compound behaviour in hydrogen matrix

Interactions between contaminants in the same cylinder have also been shown to be possible. Such cross reactivity and potential by-products need to be understood and differentiated from stability issues. Some of the results of the stability of components varied with and without water in the cylinder as seen with the formic acid amount fraction. Additionally, the presence of ammonia in the MetroHyVe 2 study for the activity 2.2 showed reaction of ammonia with formaldehyde and formic acid. This would mean that if an HRS has both ammonia and formaldehyde or formic acid in the sample gas these contaminants would react and not be likely to be measurable. Further research and fundamental studies on compounds behaviour in gas phase are required to better understood real life observation and feedback to the industry.

5.4. Gas cylinder performance testing and verification

As reported in section 4, the effect of repetitive sampling using the same cylinder seems to show degradation to the internal treatment in a similar way to aging of the cylinder. It highlighted the importance of further investigation on cylinders. Several studies should investigate aging cylinders more finely (e.g., 1, 2-, 3-, 5- and 7-year-old), repetitive use (e.g., 1, 5, 10 and 20 samplings), multiples cylinders from one production batch or between batch cylinder performance.

These tests are critical for the implementation of good practice for hydrogen fuel sampling and for enhanced knowledge on gas cylinder performance. These studies would require suitable facilities and competence as available at a national metrology laboratory. It would require developing an enhanced and optimised facility that would be able to be accessible at reasonable cost and reliable. Such a facility would allow gas manufacturer to progress their knowledge further on gas cylinder performance and hydrogen fuel sampling operators to verify the performance of their cylinders at specific times.

6. References

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7. Annex A – Analytical and preparation methods

The preparation methods and analytical analysis methods for the MetroHyVe 2 A3.1.6 and A3.1.7 are summarised below.

7.1. Analytical method

The ammonia amount fraction was analysed using selected ion flow tube coupled with mass spectrometry (SIFT-MS), Voice 200 Ultra (Anatune, UK). The reagent ion used was O_2^+ and the reaction product measured was NH_3^+.

The formaldehyde amount fraction was analysed using SIFT-MS, Voice 200 Ultra (Element, UK). The reagent ion used was H_3O^+ and the reaction product measured was CH_3O^+.

The formic acid amount fraction was analysed using SIFT-MS, Voice 200 Ultra (Element, UK). The reagent ion used was H_3O^+ and the reaction product measured was $HCOOH_2^+$.

The hydrogen chloride amount fraction was analysed using SIFT-MS, Voice 200 Ultra (Element, UK). The reagent ion used was NO_2^- and the reaction product measured was $^{35}Cl^-$.

The sulphur amount fraction was measured on a gas chromatograph coupled with a sulphur chemiluminescence detector (GC-SCD) (Agilent, UK). The method used a HP-1 column (60 m x 0.530 mm) with helium carrier. The sample loop size used for injection was 5 ml.

For this study conducted a fully Sulfinert® treated injection system was used for all samples and standards. The regulator and tubing connections from the sample cylinder to the analyser where the same for all samples and standards. For all but 4 of the cylinder's types the injection system could use an NPL minimum dead volume connecter attached to an internal thread connection of the cylinder valve. The different conditions for connections from the cylinder valve to the injection system tubing and regulator were as follows; the Sulfinert® stainless steel cylinder instead used direct Sulfinert® treated Swagelok connections to the cylinder; the Aculife III and AlphaTech cylinders used a Sulfinert® treated DIN 477 No.1 connector and the ALD-coated steel cylinder used a Sulfinert® treated DIN477 No. 14 connector.

7.2. Preparation of cylinders

Before filling all cylinders were evacuated for at least 14 hours on a high vacuum system achieving a vacuum of at least 5 x 10^{-7} mBar. The ALD-coated steel cylinder that was only evacuated to 3 x10^{-3} mBar for 3 hours due to manufacturer recommendations.

All samples were prepared gravimetrically by dilution of NPL PRMs in high purity hydrogen (99.9999 %, BIP+, Air Products, US) according to ISO 6142-1 [7]. This was done using a well purged gas transfer line. The gas transfer line used was a 1/16" (Thames Restek, UK) treated tubing with Swagelok® connections with a minimum-dead-volume (MDV) connection (developed by NPL) at each end to connect to the cylinder. All components used were treated with Silconert® passivation (Thames Restek, UK). Purging was done via cyclic pressure purging a minimum of six times at each end of the filling line (the line was pressurised with filling gas then depressurised to displace residual air from the line). The cylinder used to prepare each sample was weighed against a tare cylinder (of equal size and shape) on a top pan electronic balance of type XPE26003LC (Mettler Toledo, US) using an automated weighing facility (KRISS, SK). The sample cylinders were weighed once they had been evacuated (before gas addition) and again after each addition. The mass of the PRM transferred was calculated using the mass difference between the cylinder before and after gas transfer [8]. The cylinders were rolled for 2 hours to homogenise the gas mixture after the preparation.

The cylinders were split into two different compositions due remove prevent the more basic ammonia reacting with the acidic components (formic acid, formaldehyde, HCl). The two sets were then made first without water present and then once the stability study on this initial set was finished a second set of mixtures were re-made in the cylinders with water present to teste the effect, if any, on the component stability. The amount fractions of the components in the mixtures analysed in the MetroHyVe 2 A3.1 studies are summarised in Tables 8 and 9 below.

Table 8: Target amount fractions for the stability testing cylinders set 1 (acidic components). All cylinders were produced in matrix hydrogen.

Component	Amount fraction target (µmol/mol)
Formic acid	0.4
Formaldehyde	0.4
Hydrogen sulphide	0.008
Hydrogen chloride	0.1
Water (when present)	5
Nitrogen (tracer)	1000

Table 9: Target amount fractions for the stability testing cylinders set 2 (basic components). All cylinders were produced in matrix hydrogen.

Component	Amount fraction target (µmol/mol)
Ammonia	0.4
Water (when present)	5
Nitrogen (tracer)	300

8. Annex B – tables of results

The tables of results from the reactive components from the MetroHyVe 2 A3.1.6 and A3.1.7 short term stability studies are presented below.

Table 10: Stability results of hydrogen chloride without water

		measured amount fraction (µmol/mol)			
Cylinder ID	Gravimetric amount fraction (µmol/mol)	Time 0-1 day	Time 7-8 dyas	Time 35-36 days	Time 119-120 days
Untreated SGS	0.112 ± 0.001	< 0.015	< 0.015	< 0.015	< 0.02
DB Gold	0.100 ± 0.001	0.078 ± 0.026	0.084 ± 0.027	0.106 ± 0.032	0.094 ± 0.031
Untreated SGS	0.105 ± 0.001	0.043 ± 0.019	< 0.015	< 0.015	< 0.02
SPECTRA-SEAL	0.093 ± 0.001	0.099 ± 0.027	0.120 ± 0.032	0.091 ± 0.028	0.088 ± 0.029
H2 Mobility	0.092 ± 0.001	0.029 ± 0.016	0.039 ± 0.019	< 0.015	< 0.02

Stainless steel Sulfinert®	0.091 ± 0.002	0.066 ± 0.016	0.062 ± 0.024	0.059 ± 0.023	< 0.02
ALD-Coated steel	0.100 ± 0.001	0.044 ± 0.019	0.054 ± 0.022	0.051 ± 0.024	< 0.02
Aculife III	0.102 ± 0.001	0.055 ± 0.022	0.051 ± 0.022	0.038 ± 0.02	< 0.02
AlphaTech	0.089 ± 0.001	0.024 ± 0.016	0.035 ± 0.019	0.041 ± 0.022	< 0.02
White Top	0.105 ± 0.001	0.020 ± 0.014	0.057 ± 0.022	0.032 ± 0.019	0.033 ± 0.024
Manganese steel	0.104 ± 0.001	0.045 ± 0.02	< 0.015	< 0.015	< 0.02

Table 11: Stability results of formic acid without water

		measured amount fraction (µmol/mol)			
Cylinder ID	Gravimetric amount fraction (µmol/mol)	Time 2-3 days	Time 9-10 days	Time 29-31 days	Time 121-123 days
Untreated SGS	0.422 ± 0.003	0.167 ± 0.009	0.133 ± 0.008	0.109 ± 0.008	0.064 ± 0.006
DB Gold	0.415 ± 0.003	0.367 ± 0.015	0.328 ± 0.015	0.381 ± 0.018	0.345 ± 0.014
Untreated SGS	0.396 ± 0.003	0.21 ± 0.010	0.185 ± 0.01	0.166 ± 0.011	0.118 ± 0.008
SPECTRA-SEAL	0.385 ± 0.003	0.347 ± 0.015	0.307 ± 0.014	0.385 ± 0.017	0.368 ± 0.015
H2 Mobility	0.444 ± 0.004	0.338 ± 0.015	0.305 ± 0.013	0.336 ± 0.019	0.285 ± 0.014
Stainless steel Sulfinert®	0.414 ± 0.008	0.398 ± 0.023	0.351 ± 0.015	0.414 ± 0.018	0.417 ± 0.019
ALD-coated steel	0.385 ± 0.003	0.257 ± 0.012	0.218 ± 0.011	0.243 ± 0.014	0.208 ± 0.011
Aculife III	0.397 ± 0.003	0.287 ± 0.013	0.243 ± 0.012	0.282 ± 0.015	0.296 ± 0.016
AlphaTech	0.389 ± 0.004	0.295 ± 0.013	0.246 ± 0.012	0.302 ± 0.016	0.271 ± 0.013
White Top	0.400 ± 0.003	0.232 ± 0.012	0.189 ± 0.011	0.235 ± 0.013	0.168 ± 0.009
Manganese steel	0.456 ± 0.004	< 0.02	< 0.02	< 0.02	< 0.02

Table 12: Stability results of formaldehyde without water

Final Table		measured amount fraction (µmol/mol)			
Cylinder ID	Gravimetric amount fraction (µmol/mol)	Time 2-3 days	Time 9-10 days	Time 29-31 days	Time 127 days
Untreated SGS	0.371 ± 0.021	0.362 ± 0.017	0.39 ± 0.018	0.406 ± 0.019	0.392 ± 0.018
DB Gold	0.398 ± 0.022	0.423 ± 0.020	0.441 ± 0.021	0.466 ± 0.021	0.445 ± 0.021

Untreated SGS	0.407 ± 0.023	0.432 ± 0.020	0.467 ± 0.023	0.474 ± 0.021	0.461 ± 0.021
SPECTRA-SEAL	0.455 ± 0.025	0.477 ± 0.021	0.504 ± 0.023	0.543 ± 0.024	0.500 ± 0.023
H2 Mobility	0.463 ± 0.027	0.508 ± 0.023	0.519 ± 0.025	0.513 ± 0.023	0.498 ± 0.023
Stainless steel Sulfinert®	0.391 ± 0.022	0.414 ± 0.027	0.434 ± 0.020	0.442 ± 0.021	0.402 ± 0.019
ALD-Coated steel	0.431 ± 0.024	0.429 ± 0.020	0.449 ± 0.021	0.445 ± 0.02	0.376 ± 0.018
Aculife III	0.411 ± 0.023	0.447 ± 0.020	0.474 ± 0.021	0.489 ± 0.023	0.473 ± 0.022
AlphaTech	0.562 ± 0.032	0.608 ± 0.025	0.636 ± 0.027	0.637 ± 0.027	0.632 ± 0.028
White Top	0.443 ± 0.025	0.493 ± 0.022	0.555 ± 0.024	0.525 ± 0.023	0.516 ± 0.023
Manganese steel	0.463 ± 0.031	0.423 ± 0.020	0.423 ± 0.025	0.398 ± 0.019	0.239 ± 0.014

Table 13: Stability results of hydrogen sulphide without water, greyed out cells are measurements that have been removed due to technical reasons.

		measured amount fraction (nmol/mol)			
Cylinder ID	Gravimetric amount fraction (μmol/mol)	Time 2-3 days	Time 8-9 days	Time 28-29 days	Time 120 days
Untreated SGS	9.111 ± 0.137	9.956 ± 0.509	9.180 ± 0.271	8.023 ± 0.481	8.083 ± 1.769
DB Gold	9.263 ± 0.137	10.683 ± 0.385	9.625 ± 0.744	8.983 ± 1.040	8.952 ± 1.979
Untreated SGS	9.725 ± 0.143	10.105 ± 0.287	9.802 ± 0.345	8.526 ± 0.946	7.745 ± 0.920
SPECTRA-SEAL	9.867 ± 0.144	1.423 ± 0.180	0.642 ± 0.357	< 0.5	< 0.5
H2 Mobility	8.462 ± 0.146	5.852 ± 0.577	5.053 ± 0.408	2.577 ± 0.739	1.621 ± 1.123
Stainless steel Sulfinert®	7.765 ± 0.227	8.480 ± 0.691	7.843 ± 0.697	6.471 ± 1.011	6.243 ± 1.618
ALD-Coated steel	9.855 ± 0.145	Only OCS measured	Only OCS measured	Only OCS measured	Only OCS measured
Aculife III	9.317 ± 0.138	8.492 ± 0.342	5.231 ± 0.223	4.397 ± 0.725	5.493 ± 1.096
AlphaTech	9.128 ± 0.152	5.298 ± 0.560	2.294 ± 0.300	0.843 ± 0.660	< 0.5
White Top	8.827 ± 0.132	9.492 ± 0.558	9.279 ± 0.552	-	6.944 ± 1.383
Manganese steel	9.314 ± 0.151	8.120 ± 0.281	6.632 ± 0.185	2.361 ± 0.739	< 0.5

Table 14: Summary of results of formic acid result with water

Final Table		measured amount fraction (µmol/mol)		
Cylinder ID	Gravimetric amount fraction (µmol/mol)	Time 0-4 days	Time 9 -15 days	Time 143-151 days
Untreated SGS	0.390 ± 0.003	0.381 ± 0.043	0.377 ± 0.035	0.296 ± 0.027
DB Gold	0.382 ± 0.003	0.411 ± 0.040	0.391 ± 0.038	0.352 ± 0.027
Untreated SGS	0.385 ± 0.003	0.392 ± 0.035	0.365 ± 0.042	0.280 ± 0.023
SPECTRA-SEAL	0.373 ± 0.003	0.381 ± 0.041	0.391 ± 0.041	0.343 ± 0.027
H2 Mobility	0.459 ± 0.027	0.294 ± 0.026	0.267 ± 0.033	0.218 ± 0.02
Stainless steel Sulfinert®	0.406 ± 0.009	0.371 ± 0.033	0.399 ± 0.038	0.351 ± 0.027
ALD-Coated steel	0.408 ± 0.003	0.361 ± 0.032	0.388 ± 0.036	0.293 ± 0.025
Aculife III	0.409 ± 0.003	0.385 ± 0.035	0.384 ± 0.036	0.320 ± 0.028
AlphaTech	0.365 ± 0.004	0.321 ± 0.035	0.328 ± 0.033	0.267 ± 0.029
White Top	0.421 ± 0.003	0.390 ± 0.034	0.385 ± 0.038	0.367 ± 0.03
Manganese steel	0.420 ± 0.004	< 0.02	< 0.02	< 0.02
SPECTRA-SEAL >5 years old	0.402 ± 0.003	0.385 ± 0.035	0.387 ± 0.044	0.310 ± 0.023
SPECTRA-SEAL >5 years old	0.389 ± 0.003	0.361 ± 0.034	0.379 ± 0.039	0.305 ± 0.026
SPECTRA-SEAL > 3 samplings	0.395 ± 0.003	0.367 ± 0.035	0.364 ± 0.038	0.322 ± 0.025
SPECTRA-SEAL > 3 samplings	0.387 ± 0.003	0.342 ± 0.039	0.332 ± 0.034	0.306 ± 0.027
Stainless steel Sulfinert® > 5 years old	0.441 ± 0.006	0.052 ± 0.017	0.038 ± 0.018	0.043 ± 0.010

Table 15: Summary of formaldehyde result with water

Final Table		measured amount fraction (µmol/mol)			
Cylinder ID	Gravimetric amount fraction (µmol/mol)	Time 0-4 days	Time 9-16 days	Time 86-92 days	Time 143-151 days
Untreated SGS	0.424 ± 0.024	0.428 ± 0.048	0.432 ± 0.044	0.388 ± 0.058	0.417 ± 0.037
DB Gold	0.438 ± 0.025	0.437 ± 0.043	0.418 ± 0.047	0.388 ± 0.053	0.419 ± 0.036
Untreated SGS	0.395 ± 0.022	0.393 ± 0.041	0.396 ± 0.043	0.383 ± 0.056	0.378 ± 0.033
SPECTRA-SEAL	0.389 ± 0.022	0.393 ± 0.042	0.382 ± 0.040	0.320 ± 0.051	0.365 ± 0.034
H2 Mobility	0.459 ± 0.027	0.426 ± 0.047	0.432 ± 0.046	0.380 ± 0.065	0.402 ± 0.036
Stainless steel Sulfinert®	0.408 ± 0.028	0.404 ± 0.041	0.418 ± 0.046	0.414 ± 0.064	0.392 ± 0.037
ALD-Coated steel	0.433 ± 0.024	0.410 ± 0.044	0.418 ± 0.043	0.340 ± 0.048	0.363 ± 0.033
Aculife III	0.416 ± 0.024	0.402 ± 0.043	0.396 ± 0.042	0.408 ± 0.067	0.413 ± 0.036
AlphaTech	0.418 ± 0.024	0.413 ± 0.044	0.403 ± 0.044	0.402 ± 0.06	0.387 ± 0.035
White Top	0.414 ± 0.012	0.391 ± 0.039	0.382 ± 0.046	0.425 ± 0.067	0.370 ± 0.033

Manganese steel	0.409 ± 0.012	0.388 ± 0.039	0.385 ± 0.042	0.371 ± 0.06	0.348 ± 0.033
SPECTRA-SEAL >5 years old	0.401 ± 0.023	0.390 ± 0.043	0.385 ± 0.042	0.385 ± 0.06	0.349 ± 0.034
SPECTRA-SEAL >5 years old	0.391 ± 0.022	0.372 ± 0.040	0.371 ± 0.043	0.309 ± 0.047	0.330 ± 0.033
SPECTRA-SEAL > 3 samplings	0.395 ± 0.022	0.375 ± 0.044	0.375 ± 0.046	0.363 ± 0.054	0.342 ± 0.035
SPECTRA-SEAL > 3 samplings	0.404 ± 0.023	0.393 ± 0.042	0.385 ± 0.038	0.332 ± 0.053	0.331 ± 0.031
Stainless steel Sulfinert® > 5 years old	0.434 ± 0.026	0.221 ± 0.027	0.220 ± 0.028	0.161 ± 0.033	0.159 ± 0.021

Table 16: Summary of hydrogen sulphide with water

		measured amount fraction (nmol/mol)			
Cylinder ID	Gravimetric amount fraction (nmol/mol)	Time 0-4 days	Time 8 -15 days	Time 23-29 days	Time 113-120 days
Untreated SGS	7.393 ± 0.071	8.194 ± 0.503	7.120 ± 0.448	6.787 ± 0.306	6.920 ± 0.318
DB Gold	7.532 ± 0.072	8.146 ± 0.461	7.529 ± 0.312	7.229 ± 0.389	7.727 ± 0.474
Untreated SGS	7.820 ± 0.073	7.824 ± 0.477	7.654 ± 0.377	7.112 ± 0.409	7.560 ± 0.574
SPECTRA-SEAL	8.013 ± 0.074	5.232 ± 0.373	4.091 ± 0.274	2.649 ± 0.251	1.017 ± 0.164
H2 Mobility	7.894 ± 0.13	4.935 ± 0.348	3.536 ± 0.321	3.080 ± 0.275	0.672 ± 0.202
Stainless steel Sulfinert®	7.671 ± 0.214	7.531 ± 0.672	7.516 ± 0.279	6.540 ± 0.340	7.676 ± 0.392
ALD-Coated steel	7.731 ± 0.071	4.664 ± 0.544	0.688 ± 0.165	0.143 ± 0.276	0.064 ± 0.129
Aculife III	7.555 ± 0.071	5.368 ± 0.281	2.856 ± 0.368	4.167 ± 0.291	6.604 ± 1.471
AlphaTech	7.936 ± 0.103	4.618 ± 0.464	3.188 ± 0.233	1.692 ± 0.171	0.663 ± 0.134
White Top	7.986 ± 0.074	7.818 ± 0.373	7.531 ± 0.344	7.048 ± 0.344	8.547 ± 0.42
Manganese steel	8.028 ± 0.090	7.913 ± 0.385	7.420 ± 0.270	6.648 ± 0.32	5.024 ± 0.209
SPECTRA-SEAL >5 years old	7.567 ± 0.072	6.019 ± 0.313	3.109 ± 0.101	1.985 ± 0.110	0.264 ± 0.108
SPECTRA-SEAL >5 years old	7.615 ± 0.073	2.407 ± 0.189	< 0.5	< 0.5	< 0.5
SPECTRA-SEAL > 3 samplings	7.525 ± 0.073	1.147 ± 0.223	< 0.5	< 0.5	< 0.5

SPECTRA-SEAL > 3 samplings	7.280 ± 0.072	0.990 ± 0.16	< 0.5	< 0.5	< 0.5
Stainless steel Sulfinert® > 5 years old	6.743 ± 0.127	3.258 ± 0.324	1.409 ± 0.2	< 0.5	< 0.5

Table 17: Summary of results of ammonia without water first batch. Greyed out cells show where cylinders were not measured during additional measurement instances

		measured amount fraction (µmol/mol)				
Cylinder ID	Gravimetric amount fraction (µmol/mol)	Time 3-4 days	Time 9-10 days	Time 36 days	Time 94 days	Time 126 days
Untreated SGS	0.401 ± 0.003	0.319 ± 0.041	0.323 ± 0.040	0.365 ± 0.039	0.377 ± 0.039	0.364 ± 0.039
Untreated SGS	0.406 ± 0.003	0.252 ± 0.040	0.278 ± 0.040	0.300 ± 0.039	0.299 ± 0.039	0.310 ± 0.039
SPECTRA-SEAL	0.385 ± 0.003	0.09 ± 0.040	0.138 ± 0.039	< 0.02	< 0.02	< 0.02
DB Gold	0.391 ± 0.003	0.38 ± 0.041	0.352 ± 0.040	0.372 ± 0.039	0.367 ± 0.039	0.357 ± 0.039
White Top	0.401 ± 0.003	0.249 ± 0.040	0.199 ± 0.039	0.225 ± 0.039	0.226 ± 0.039	0.245 ± 0.039
Aculife III	0.402 ± 0.003	0.373 ± 0.042	0.321 ± 0.040	0.390 ± 0.039	0.378 ± 0.040	0.372 ± 0.039

Table 18: Summary of results of ammonia without water second batch. Greyed out cells show where cylinders were not measured during additional measurement instances

		Measured amount fraction (µmol/mol)					
Cylinder ID	Gravimetric amount fraction (µmol/mol)	Time 1 day	Time 8 days	Time 28 days	Time 125-127 days	Time 160 days	Time 188-189 days
SPECTRA-SEAL	0.409 ± 0.002	0.303 ± 0.043	0.250 ± 0.043	0.256 ± 0.043	0.265 ± 0.043		0.219 ± 0.046
H2 Mobility	0.487 ± 0.002	0.518 ± 0.044	0.519 ± 0.043	0.492 ± 0.043	0.489 ± 0.043		0.399 ± 0.047
Manganese steel	0.400 ± 0.002	0.362 ± 0.043	0.371 ± 0.043	0.369 ± 0.043	0.321 ± 0.043		0.332 ± 0.046
Stainless steel Sulfinert®	0.567 ± 0.004	0.661 ± 0.044	0.739 ± 0.044	0.644 ± 0.044	0.591 ± 0.044		0.589 ± 0.046
AlphaTech	0.365 ± 0.003	0.305 ± 0.043	0.340 ± 0.043	0.275 ± 0.043	0.463 ± 0.044	0.308 ± 0.044	0.134 ± 0.046

ALD-Coated steel	0.403 ± 0.002	0.226 ± 0.043	0.232 ± 0.043	0.162 ± 0.043	0.114 ± 0.043		0.064 ± 0.045

Table 19: Table of results of ammonia with water first batch

		measured amount fraction (µmol/mol)			
Cylinder ID	Gravimetric amount fraction (µmol/mol)	Time 0 days	Time 6 days	Time 20-21 days	Time 110-112 days
Untreated SGS	0.401 ± 0.003	0.392 ± 0.039	0.399 ± 0.018	0.359 ± 0.020	0.483 ± 0.021
Untreated SGS	0.406 ± 0.003	0.498 ± 0.021	0.397 ± 0.017	0.347 ± 0.018	0.500 ± 0.021
SPECTRA-SEAL	0.385 ± 0.003	0.359 ± 0.017	0.312 ± 0.015	0.254 ± 0.017	0.258 ± 0.014
DB Gold	0.391 ± 0.003	0.402 ± 0.018	0.366 ± 0.018	0.438 ± 0.021	0.434 ± 0.021
White Top	0.401 ± 0.003	0.430 ± 0.019	0.420 ± 0.019	0.489 ± 0.020	0.469 ± 0.021
Aculife III	0.402 ± 0.003	0.377 ± 0.018	0.418 ± 0.018	0.430 ± 0.020	0.393 ± 0.019

Table 20: Table of results of ammonia with water second batch

		measured amount fraction (µmol/mol)			
Cylinder ID	Gravimetric amount fraction (µmol/mol)	Time 3-4 days	Time 10-11 days	Time 45-46 days	Time 137-138 days
SPECTRA-SEAL	0.409 ± 0.003	0.315 ± 0.014	0.345 ± 0.013	0.312 ± 0.012	0.307 ± 0.033
H2 Mobility	0.42 ± 0.005	0.405 ± 0.014	0.374 ± 0.014	0.358 ± 0.014	0.351 ± 0.035
Manganese steel	0.424 ± 0.004	0.427 ± 0.014	0.371 ± 0.014	0.375 ± 0.014	0.308 ± 0.038
Stainless steel Sulfinert®	0.401 ± 0.008	0.387 ± 0.015	0.378 ± 0.013	0.375 ± 0.014	0.454 ± 0.047
AlphaTech	0.404 ± 0.004	0.297 ± 0.012	0.285 ± 0.012	0.248 ± 0.011	0.288 ± 0.033
ALD-Coated steel	0.405 ± 0.003	0.326 ± 0.012	0.337 ± 0.013	0.281 ± 0.012	0.308 0.038