METROLOGY for HYDROGEN VEHICLES 2

REPORT:

A2.1.2: Literature review of preparation techniques and cylinder treatments for preparation of formaldehyde and ammonia binary calibrants in hydrogen

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Summary

This report was written as part of activity 2.1.2 from the EMPIR Metrology for Hydrogen Vehicles 2 (MetroHyVe2) project. The report presents the state of the art in preparation techniques for formaldehyde and ammonia binary gas calibrants in hydrogen.

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

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Introduction

Several European laboratories are developing the capability to measure the contaminants specified in ISO 14687:2019 [1] and EN 17124:2018 [2] as part of European projects (e.g., EMPIR project 16ENG01 MetroHyVe, Horizon 2020 project HYDRAITE) or of businesses (e.g., Air Liquide, Linde). The new standard ISO 21087:2019 [3] is setting uncertainty thresholds and validation procedures to be met (e.g., relative measurement uncertainty below 20 %, trueness validation close to ISO14687:2019 threshold). A lack of gas calibrants with sufficiently low uncertainty (e.g., formaldehyde and ammonia), reference materials for validation and inter-laboratory comparison are the most urgent identified barriers before European commercial laboratories can demonstrate their compliance to ISO 21087:2019 [3] requirements and their ability to measure contaminants in ISO 14687:2019 [1].

The Metrohyve 2 project (19ENG04) evaluated and reported the needs of commercial laboratories for gas calibrants in order to be compliant with ISO21087:2019 [4]. The MetroHyVe 2 survey highlighted that formaldehyde and ammonia are part of the gas calibrants required by the industry with longer shelf-life (1-2 years).

Ammonia and formaldehyde are considered as reactive compounds and therefore are challenging to maintain stable in gas cylinders for long time period [5, 6, 7]. Therefore MetroHyVe 2 aim at studying the stability of formaldehyde and ammonia binary gas mixture in hydrogen or alternative gas matrix to provide new evidence supporting the development of new reliable gas standards.

Prior to develop and perform stability study, a literature review was investigating the current state of the art preparation techniques for static ammonia and formaldehyde binary mixtures in hydrogen. This objective is to evaluate the current practice, any advantages or drawback in order to define the best strategy for the future MetroHyVe 2 stability study on ammonia and formaldehyde in hydrogen.

The report will investigate each compound independently considering the cylinder type and the preparation method used.

Ammonia

Cylinder types

One of the key parameters in reactive compounds stability in gas cylinder is the actual gas cylinder. A literature review was carried out to investigate ammonia stability in different cylinder types. The results are summarised in Table 1.

Table1: information on ammonia stability in different cylinder types

Cylinder type (treatment supplier)	Matrix	nominal amount fraction [µmol/mol]	Summary	Reference
Aluminum Spectra-seal volume 10L (BOC)	Nitrogen	10	12 month stability within 3% uncertainty	[5]
Aculife 4 (Air Liquide)	Nitrogen	10	12 month stability within 3% uncertainty	[5]
Takachiho (Takachiho)	Nitrogen	10	12 month stability within 3% uncertainty	[5]
Stainless steel Silconert 2000 volume 1L (Restek)	Nitrogen	10	No significant instability over a year and no significant	[5]

			transfer loss on preparation	
Aluminum Spectra-seal volume 10L (BOC)	Hydrogen	0.2	Significant initial loss (above 0.1 µmol/mol)	[6]
Aluminum Luxfer SGS volume 10L (Luxfer)	Hydrogen	0.2	Significant initial loss (above 0.1 µmol/mol)	[6]

Previous studies on ammonia stability in nitrogen matrix at 10 µmol/mol showed good stability for multiple cylinder treatments: Spectra-Seal, Aculife 4, Takachiho and Silconert 2000 [5]. It is therefore considered stable over time in nitrogen matrix and in various cylinder type.

However very little information could be found on ammonia stability in hydrogen matrix in gas cylinders. Morris et al. study [6] showed large initial losses at low amount fractions. This study was unable to conclude on the actual long-term stability of ammonia in hydrogen matrix. NPL unpublished data at higher amount fraction indicated that ammonia may be stable over 12 months in cylinders. However, any preparative loss is a critical issue in the preparation of gravimetric primary gas standard.

It was, therefore, concluded that preparation techniques that can reduce the preparative losses of ammonia in hydrogen binary standards should be investigated as a higher priority than investigating various cylinder types.

Preparation techniques - ammonia

The preparation of ammonia gas mixture is normally performed starting from pure gas components (e.g., high purity ammonia gas and high purity nitrogen or hydrogen) following ISO 6142-1 [7]. Starting from pure materials allows limitation of any issues with interferences. No other gas preparation methodologies have been found starting from liquid, solid or involving reactions.

Investigation of the literature of preparation techniques able to reduce initial preparative losses highlighted few possibilities: cylinder pre-treatment or conditioning, exchange dilution method [9]. A pre-treatment technique to the gas cylinder involves exposing the cylinder to a high concentration of ammonia. It can be compared to a pickling process. After exposure of the cylinder, the normal preparation of gravimetric primary standard is carried out and may achieve closer agreement with the desired amount fraction mixture (reduced initial loss). The other method named 'Exchange dilution' involves making a high concentration mixture in the cylinder which is then used as the parent within the same cylinder. This method had been shown to reduce preparation loss of mixtures of carbon dioxide and water at µmol/mol levels [8].

These two preparative methods are foreseen to have a significant impact on the accurate preparation of ammonia in hydrogen gas standard. The MetroHyVe 2 partners will investigate them to provide new evidence on their performance and applicability for hydrogen gas calibrants.

Formaldehyde

Cylinder types

Formaldehyde is a really difficult compound to keep stable in gas cylinders. Several studies have been dedicated to formaldehyde in nitrogen and hydrogen [9,10,11,12]. A summary of the literature on formaldehyde stability in hydrogen matrix is presented in Table 2.

Table 2: Summary of literature review of formaldehyde stability in different cylinder treatment types

Cylinder type (treatment supplier)	Matrix	nominal amount fraction [µmol/mol]	Summary	Reference
Aluminum Spectra-seal 10L (BOC)	Hydrogen	10	Stability for at least 8 weeks, large discrepancies between cylinder performance	[9]
Aluminum Spectra-seal 10L (BOC)	Hydrogen	0.2	Initial loss then stable for 4 months, large discrepancies between cylinder performance	[6]
Aluminum Luxfer SGS 10L (Luxfer)	Hydrogen	0.2	Rapid loss of formaldehyde to below LOD after two weeks	[6]
Aluminum Spectra-seal 10L (BOC)	Nitrogen	10	Calculated decay rate of 1.6 nmol/mol a day	[10]
Aluminum Luxfer SGS 10L (Luxfer)	Nitrogen	2	Slow linear loss over 1 year (about 0.7% per month)	[11]
Al-Acu-VIII (Air Liquide)	Nitrogen	2	Relative loss rate of 1.2% a year	[12]
Al-Acu-IV+VIII (Air Liquide)	Nitrogen	2	1 year stability within 1% uncertainty	[12]

The formaldehyde in hydrogen stability study at 10 µmol/mol in aluminium cylinder with Spectra-Seal treatment showed short stability period and the presence of reaction products between hydrogen with the formaldehyde [9]. The studies of Panda et al. and Rhoderick et al. showed good long-term stability of formaldehyde in nitrogen matrix in multiple gas cylinders [11, 12]. These results are different from the observation in hydrogen matrix. If the instability may be caused by reaction with hydrogen matrix, the gas cylinder stability data from studies in nitrogen matrix are not as relevant as for ammonia. Therefore, the current cylinder type does not seem to influence the formaldehyde stability in nitrogen (either stable in nitrogen matrix, unstable in hydrogen matrix). The number of gas cylinder studied is quite limited for formaldehyde in hydrogen. There is a benefit to investigate the cylinder presenting good stability in nitrogen matrix (e.g., Aluminium cylinder Aculife) and new cylinder type to determine the impact of gas cylinder on the stability of formaldehyde in hydrogen gas standard.

Preparation techniques

Pure formaldehyde, a gas, is not handled commercially because it tends to polymerize exothermally and may ignite. Formaldehyde can be found as solid or in solution (formalin). The purity and the nature of formaldehyde makes the gas preparation more challenging than for ammonia.

Different preparation techniques were investigated, including preparation from paraformaldehyde [11] and trioxane [10].

The preparation of paraformaldehyde is realised by first placing paraformaldehyde within a chamber. The chamber is them evacuated to remove air and moisture. The paraformaldehyde is then heated to convert it into formaldehyde. A small amount of balance gas (in the example case nitrogen) is then added to the chamber and the resulting formaldehyde in gas mixture then transferred to the mixture cylinder [11]. The preparation of formaldehyde gas mixture using trioxane is done by first processing the trioxane into a pellet. The pellet of trioxane is then evacuated in a transfer vessel in the presence of phosphorous pentoxide to remove water and air from the trioxane. The pellet of trioxane is then heated under vacuum to convert the trioxane into formaldehyde which is transferred directly into the mixture cylinder [10].

However, Panda et al. [11] showed that the starting material didn't significantly influence the stability of the formaldehyde in nitrogen matrix. Therefore, the main contribution to the stability of the formaldehyde was related to the matrix reaction [9] and the cylinder type.

The MetroHyVe 2 partners will investigate different cylinder types (e.g Aluminium cylinder Aculife) and different matrix (e.g., helium, nitrogen and hydrogen). The aim is to determine the most suitable combination in term of gas cylinder and matrix gas to provide a new set of commercial gas calibrants to the commercial laboratories in short term.

Perspectives

The report highlights the complexity of preparing ammonia and formaldehyde binary gas calibrants in hydrogen. For ammonia, there is evidence of long-term stability at µmol/mol amount fraction over a long period of time, however, at nmol/mol amount fraction, the preparative losses require further investigation. Two preparative methods (preconditioning and exchange dilution) are foreseen to have a significant impact on the accurate preparation of ammonia in hydrogen gas standard and will be studied as part of MetroHyVe 2 project.

For formaldehyde, the report highlighted the difference in behaviour of formaldehyde in hydrogen matrix compared to nitrogen matrix. The hydrogen matrix seems to significantly impact the long-term stability of formaldehyde in the gas cylinder. The actual preparation method (using trioxane or paraformaldehyde) was not identified as a main source of instability compared to the actual matrix type (H_2, N_2) and cylinder type. Therefore, the MetroHyVe 2 project will investigate different cylinder types (e.g., Al-Acu) and different matrix (e.g., helium, nitrogen and hydrogen) with the objective to propose the most suitable combination in term of gas cylinder and matrix gas for commercial formaldehyde gas calibrants in short term.

The report highlights the importance of supporting the research and development around enhanced cylinder surface passivation or in the development of alternative calibration strategies for ammonia and formaldehyde. It would be interesting for the industry to investigate new cylinder passivation or surface that may improve the behaviour of ammonia or formaldehyde in hydrogen matrix at nmol/mol amount fraction, however, it may require longer term commitment for the development of new suitable passivation. In the short term, MetroHyVe 2 project is aiming to support pragmatic and accurate solutions adapted to hydrogen fuel quality.

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