METROLOGY for HYDROGEN VEHICLES

REPORT:

A2.3.1: Review of the available passivation treatments for gas cylinders

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.

www.metrohyve.eu

This report was written as part of activity A2.3.1 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.

This guide was written by:

H. Meuzelaar	VSL	hmeuzelaar@vsl.nl
S.T. Persijn	VSL	spersijn@vsl.nl
J.I.T. van Wijk	VSL	jvanwijk@vsl.nl
T. Bacquart	NPL	thomas.bacquart@npl.co.uk
S. Bartlett	NPL	sam.bartlett@npl.co.uk
A. Murugan	NPL	arul.murugan@npl.co.uk

Contents

Introduction

The preparation of primary reference gas mixtures and dynamic reference standards for low-level contaminants in hydrogen is essential to demonstrate traceability of hydrogen purity measurements. However, the preparation of stable gaseous reference materials of the impurities listed in ISO 14687 at the threshold specifications (see Table 1) is challenging in several different ways: some impurities will be affected by adsorption onto solid media such as cylinder walls (e.g. water and ammonia), others are at an extremely low level (e.g. 4 ppb total sulphur species) and some species are highly reactive like some of the halogenates such as HCl. Passivation of the internal cylinder surface can result in a significant reduction of the adsorption and reaction. The objective of this task is to provide a review of the possible surface passivation treatments that are available for gas cylinders (and the corresponding stability data) for all 13 gaseous impurities as specified in ISO 14687. Information gained from literature review and other projects (e.g. EMRP MetNH3 project and EMRP Biogas project) is included. This information can be used to assess the availability of cylinders that will allow stable mixtures to be produced for all ISO 14687 impurities and where the limitations are.

***Table 1** Hydrogen purity requirements as specified in ISO 14687.*

Species	Maximum Concentration (µmol/mol) (ppm)
Water	5
Total hydrocarbons	2
Oxygen	5
Helium	300
Nitrogen/Argon	100
Carbon Dioxide	2
Carbon Monoxide	0.2
Total sulphur compounds	0.004
Formaldehyde	0.01
Formic acid	0.2
Ammonia	0.1
Total halogenated compounds	0.05

Surface passivation treatments

Surface passivation treatments that are available for gas cylinders are reviewed for all 13 gaseous ISO 14687 impurities.

Impurities are classified as:

- non-critical: no specific issues are expected (taking in consideration the relatively high uncertainties allowed for H_2 purity analysis) and most available treatments are expected to perform fine.
- critical: adsorption and/or stability issues expected
- very critical: reactive impurities

In literature, data is mostly available for gas standards in nitrogen and air and this has been included here just like some other matrices such as biogas. Unfortunately, very limited data is available for standards in hydrogen. Table 2 summarizes the results from the review of treatments for the ISO 14687 impurities and the threshold specifications.

***Table 2** Candidate cylinder surface treatment for all gaseous ISO 14687 impurities.*

Species	Maximum amount fraction (µmol/mol)	Classification	Candidate treatments
Water	5	Critical	SilcoNert 2000 and in particular Dursan coatings reduce the adsorption of water on the surface [4]. Drawback of such coated cylinders is the high price and typically small volume of the stainless-steel sample cylinders up 3.8 litre. Alternative: Some NMI's supply water as CGM instead of PRM as strong initial losses are observed but long-term stability is typically good.
Total hydrocarbons	2	Non-critical ($\leq C_7$) Critical ($>C_7$)	30 component hydrocarbon mixture in air was tested with individual concentrations at 3-7 ppb in 10 L aluminium cylinders (Quantum treatment from Air Products Belgium) [7]. Results showed that above C_7 adsorption losses become more and more an issue. Note that for high carbon numbers the maximum concentration in the mixture is limited by the pressure in the cylinder to avoid condensation.
Oxygen	5	Critical	Reactivity wise: oxygen in presence of hydrogen will make water. Passivation or special treatment may be investigated otherwise it will be difficult to measure oxygen totally as water is another impurity.

Helium	300	Non-critical	
Nitrogen/ Argon	100	Non-critical	
Carbon Dioxide	2	Non-critical	
Carbon Monoxide	0.2	Critical	In the Euramet 1220 comparison CO was prepared in H_2 at nominal 0.1 and 1 ppm [5] by Linde and Air Liquide. Both used a 10 L aluminium cylinder with stainless steel outlet. The passivation treatment was not stated. For the 1 ppm mixtures, one cylinder showed a loss of 0.064 ppb/day (initial concentration 1.00 ppm). The other cylinder (initial concentration 0.985 ppm) showed no significant degradation during the duration of the comparison (2 years). For the 0.1 ppm mixtures, one cylinder showed a loss of 0.029 ppb/day (initial concentration 85.5 ppb). The other cylinder (initial concentration 99.9 ppb) showed no significant degradation during the duration of the comparison. For CO in general aluminium cylinders are preferred over stainless steel. However, in aluminium also stability issues exist (in particular in air) as was shown in the recent key comparison CCQM-84 [6]. The CO concentration (nominal 350 ppb in air) increased 1-2% in the 8 months after preparation (10 L, Luxfer) after which it was stable in the following 10 months.
Total sulphur compounds	0.004	Very critical	In the Euramet 1220 comparison H_2S was prepared in H_2 at nominally 1 ppm [5] using a 10 L aluminium cylinder with stainless steel outlet. The passivation treatment was not stated. One of these cylinders showed a loss of 0.12 ppb/day (initial concentration 0.66 ppm). The other cylinder (initial concentration 0.95 ppm) showed no significant degradation during the duration of the comparison (2 years). In the EMRP Biogas project short term stability studies (up to 11 days) have been performed in sample cylinders [10]. The tested sulphur compounds were hydrogen sulphide (H_2S), carbon sulphide (COS), methyl mercaptan, dimethylsulfide (DMS), dimethyldisulfide (DMDS) and tetrahydrothiophene at concentrations of a few ppm. Electropolished cylinders were tested for all

			except DMS and showed good stability. Sulfinert cylinders were tested for all except COS and H_2S and showed good stability. Silonite coated cylinder were tested for all except COS and H_2S and showed good stability Teflon coated cylinder were tested for all except DMDS and showed strong losses for most components. A study was performed to assess the initial losses of low concentration hydrogen sulphide (H_2S) within cylinders each with a different passivation technique. Gas mixtures of nominally 10 ppb H_2S in nitrogen were gravimetrically prepared in cylinders with the following passivation treatments: - Performax - PB - Spectraseal Analysis was undertaken the day after preparation by comparison of analyte response of each gas mixture with a dynamically-generated reference standard of similar concentration. The results indicated that a large loss of H_2S had occurred within all cylinders, however the loss was slightly larger in the cylinder with the Performax passivation. A significant loss was indicated in the cylinder with PB passivation and the cylinder with Spectraseal passivation experienced the lowest loss. However the uncertainties associated with all three measurement results overlap greatly so no conclusive results as to which passivation treatment is most suitable to minimise loss of H_2S at ppb-level can be made.
Formaldehyde	0.01	Very critical	Stability issues are expected in H_2 irrespective of the passivation treatment used due to the reaction with H_2. Formaldehyde was observed as unstable in hydrogen however the surface of the cylinders was suspected to act as catalyst. Experiments at 10 µmol/mol in Spectraseal cylinders showed decay in formaldehyde amount fraction. More interestingly, the decay was strongly dependent on the Spectraseal cylinder itself. Spectraseal cylinder pre-selection may be a prerequisite. Other cylinder pre-treatments showed better results than Spectraseal: Silconert 2000, Sulfinert and Performax with more than 80 % stability over 1 month at 1 µmol/mol formaldehyde in hydrogen.

			Aculife VIII (Scott Specialty Gases) [2] shows good stability down to 500 ppb in N_2. Formaldehyde measurements with SilcoNert 2000 coated sampling lines showed good results [3]. Therefore SilcoNert-coated, Sulfinert, Performax or pre-selected Spectraseal cylinders might be the best suitable option for formaldehyde gas standards.
Formic acid	0.2	Very critical	Linde supplies formic acid in hydrogen mixtures. VSL tested such a mixture (10 ppm) and it is reasonably stable over a 5-year period. NPL has nice stability data at 50 / 100 ppm in a Spectraseal cylinder. However, lower amount fractions seem to be more challenging: 0.3 ppm seems to decrease significantly over a 3 months period.
Ammonia	0.1	Very critical	Within the EMRP MetNH3 project several types of cylinders were tested for both 10 ppm and 100 ppm mixtures in nitrogen (see e.g. [8]). Best results were obtained for SilcoNert 2000 coated cylinders for which no losses were observed. Relatively good performance was also obtained for Spectraseal cylinders (BOC Linde) and cylinders from Takachiho. Preliminary results obtained by NPL showed that mixtures at both 10 ppm and 1 ppm seemed nicely stable. However, the same can not be said for mixtures prepared at 0.1 ppm. A low amount fraction mixture was prepared, but no signal was measured. However, it is still unclear if this is due to the analyser's LOD or instability of the mixture.
Total halogenated compounds	0.05	Very critical	In the EMRP Biogas project 10 ppm HCl in N_2 was prepared by NPL [9] in cylinders from Air Products called 'HCl passivated cylinders'. Normal preparation led to high losses. On the other hand, preparing first 100 ppm, reducing the pressure and topping with nitrogen led to much lower losses. 6-month stability was demonstrated. Takachiho T-Coat-II^{TM} [1] was shown to provide at least 1 year stability at 80 ppm HCl in N_2 and promising results at 5 ppm (limited data presented). SilcoNert 2000 coating was found suitable for HCl

			but not HF analysis [3]. The same is therefore probably also valid for gas standards in cylinders with these types of coatings.

References

[1] K. Nishi, T. Hayase, T. Nakanoya, J.Hashimoto, and Y. Yoshida, Preparation of Stable Hydrogen Chloride Standard Gases at Low Concentrations, 8thAPMP/TCQM Gas CRM Workshop, June 10th, 2010

[2] Formaldehyde Calibration Standards, https://www.scottecatalog.com/PDFFiles.nsf/7295b1c05fa9e8e38525667c00412c82/17b5c97fc9211d1785256dea0055e09d/$FILE/FormaldehydeMixes1122.1.pdf

[3] B. Marshik, Material and Process Material Conditions for Successful of Extractive Sampling Techniques, EPA Region 6 - 25th Annual Quality Assurance Conference October 21st, 2015 https://www.epa.gov/sites/production/files/2015-11/documents/c15-marshik-p2.pdf

[4] D. Smith, Contact Angle Evaluation of SilcoTek Depositions, White paper available from the Silcotek website

[5] T. Bacquart, A.M.H. van der Veen, S. Bartlett, H. Ent, J.I.T. van Wijk, M.D. Minarro, R.E. Hill-Pearce, P.J. Brewer, R.J.C. Brown, A.S. Brown, A., Murugan, NPL Report ENV 16, January 2017, ISSN: 2059-6030

[6] J. Lee, D. Moon, J. Lee, J. Lim, B. Hall, P., Novelli, P., et al., International comparison CCQM-K84—carbon monoxide in synthetic air at ambient level. Metrologia, 54(1A), 08016. (2017)

[7] R.J.P. Grenfell, M.J.T. Milton, A.M. Harling, G. M. Vargha, C. Brookes, P.G. Quincey, P. T Woods, P. T. Standard mixtures of ambient volatile organic compounds in synthetic and whole air with stable reference values. Journal of Geophysical Research: Atmospheres, 115 (D14). 2010

[8] J.I.T van Wijk, D. Bossaert, V. Ferracci, E. Amico di Meane, N. A. Martin, D1.1.7 Report on the stability study of the NH_3 mixtures in cylinders, MetNH3 project (2017)

[9] S.T. Persijn, N. Allen, Report on the comparison of the measurement methods for HCl in biogas, Deliverable 2.3.13, Biogas project (2017)

[10] K. Arrhenius, H. Yaghooby, L. Rosell, O. Büker, L, Culleton,S. Bartlett, et al.,. Suitability of vessels and adsorbents for the short-term storage of biogas/biomethane for the determination of impurities–Siloxanes, sulfur compounds, halogenated hydrocarbons, BTEX. Biomass and Bioenergy, 105, 127-135 (2017).