Publishable Summary for 16ENG01 MetroHyVe
Metrology for hydrogen vehicles

Overview

This project was in great demand by the hydrogen industry, such as by hydrogen vehicle manufacturers including BMW, Daimler and Toyota, hydrogen refuelling station (HRS) operators, gas producers and standardisation bodies. A large hydrogen infrastructure is currently under development across Europe. However the hydrogen industry is required to meet certain measurement requirements, set by European legislation that previously could not be followed due to the lack of available methods and standards. This project was funded to address these issues and to develop new metrology infrastructure that aims to support the safe use of hydrogen in refuelling stations for the transport sector. The project was the first large scale project of its kind to tackle such measurement challenges in hydrogen flow metering, hydrogen quality assurance, hydrogen quality control and hydrogen sampling. The project provides the first traceable Primary Standard for flow metering to allow accurate calculating of hydrogen dispensed into vehicles from refuelling stations and development of new sampling and hydrogen purity methods as required by ISO 14687 to allow station operators to check that quality of hydrogen does not damage end-user fuel cell vehicles.

Need

In order to determine the main measurement needs for hydrogen industry, a survey was undertaken by NPL to understand the measurement challenges that this industry faced. The survey involved key stakeholders of the hydrogen industry including hydrogen producers, station operators, automotive manufacturers and standardisation bodies and the results clearly demonstrated that there were four key technical measurement challenges that prevented a hydrogen economy from growing in Europe:

- It was not possible to accurately calculate the amount of hydrogen dispensed when filling hydrogen into a fuel cell vehicle and therefore customers were not able to be charged correctly when buying hydrogen from HRS.
- Hydrogen provided by the refuelling stations would need to meet the hydrogen purity specifications of ISO 14687/EN 17124; however no laboratory in the world could perform all of these measurements under accreditation.
- HRSs would typically need to install instruments that could continuously monitor key impurities online to ensure harmful impurities did not reach the fuel cell of vehicles; these instruments were in development but had not yet been tested or validated.
- There had been no verified techniques that could be followed, or validated sampling vessels available, for when HRSs sampled hydrogen and sent it to laboratories for purity analysis. Thus there was a high risk that the sample received by the laboratory was not representative of the hydrogen dispensed into vehicles.

Objectives

The original aim of this project was to develop metrology that will support the safe use of hydrogen in refuelling stations for the transport sector. The specific objectives were:

1. Flow metering – To develop a metrological framework for testing hydrogen meters used to measure the mass of hydrogen dispensed into a fuel cell vehicle from a refuelling station and support laboratories by providing a good practice guide describing the calibration and validation of flow meters used at HRSs. The metrological and technical requirements stipulated in OIML R 139-1 and international standard SAE J2601 - Fuelling Protocols for Light Duty Gaseous Hydrogen Surface Vehicles should be followed, with a target accuracy of 1 %.
2. Hydrogen quality assurance – To support hydrogen purity testing as specified in ISO 14687 by developing traceable offline gas analysis methods, stable and accurate primary reference gas mixtures

and the metrological tools to enable the introduction of low cost gas analysers suitable for use by commercial gas analysis laboratories. An interlaboratory comparison will be held to allow commercial laboratories to prove their competency in hydrogen purity testing which will allow them to gain evidence for obtaining accreditation for this service. In addition, to develop a robust method for accurately performing online measurement of particulates (to determine whether levels are above or below 1 mg/kg) in hydrogen provided at the refuelling station, as specified in ISO 14687.

3. Hydrogen quality control – To perform purity measurements of hydrogen following the implementation of quality control techniques specified in ISO 19880-8 and validate continuous online hydrogen purity analysers for measuring canary species (the key impurities that guarantee global quality of the hydrogen) at the HRS. A good practice guide will be developed for the use and calibration of hygrometers for online water analysis. Low cost sensors will be investigated for use at hydrogen refuelling stations for performing online monitoring of impurities for quality control.

4. Sampling – To develop a robust protocol for taking a representative sample of hydrogen gas from a refuelling station and testing suitability of high pressure sampling vessels for delivering hydrogen to gas analysis laboratories for offline purity analysis; as required by ISO 14687.

5. Creating impact – To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain (accredited laboratories, instrument manufacturers), standards developing organisations (ISO, CEN/CENELEC) and end users (hydrogen industry, vehicle manufacturers and suppliers).

Progress beyond the state of the art

The state-of-the-art for the objectives above and the outcomes from this project to go beyond this are:

Flow metering – At the start of the project there was no capability for calibrating hydrogen flow meters to be used at HRSs for monitoring the amount of hydrogen dispensed into the vehicle up to pressures of 875 bar (required for stations providing hydrogen at nominal working pressures of 700 bar). The project has developed Primary Standards that have been tested at an operational refuelling station and are now used by the hydrogen industry to calibrate and verify flow meters with hydrogen at a nominal working pressure of 700 bar. The project partners have also developed new methods which allow non-flammable substances to be used to calibrate these flow meters such as nitrogen, air or water, making these tests ultimately safer.

Hydrogen quality assurance –Hydrogen purity laboratories have been unable to provide traceable ISO 14687 hydrogen purity measurements because the methods and standards have not been developed for all of the impurities specified. The project has developed the missing methods and standards including for the low level reactive species such as ammonia, formic acid, formaldehyde and hydrochloric acid. This information will be provided to ISO TC 197 at the next meeting of WG27 to support any future revision of ISO 14687 if planned. The methods and standards have been provided to hydrogen industry by reports, peer reviewed papers, products and services.

Hydrogen quality control – Three online hydrogen purity analysers had been developed as part of the project, capable of rapid measurement of hydrogen sulphide, water, carbon dioxide and/or oxygen. These hydrogen purity analysers utilised different measurement technologies and can now be installed at HRSs as part of quality control strategies. A comparison has taken place at NPL to test performance of five commercial online purity analysers; the testing was complete, and feedback provided back to the manufacturers to advise on inaccuracies and other limitations.

Sampling – The issue of correct sampling is a common topic among the hydrogen industry as it is possible that samples of hydrogen contain impurities (such as water and air) caused by bad sampling techniques. The project performed robust tests on sampling (both particles and gas) in order to develop a good practice guide which provided a protocol for correct sampling at HRSs and selection criteria for sampling vessels. Commercial sampling methods for gas and particulates were tested; these methods were reported in a good practice guide and shown at two workshops for hydrogen sampling held at NPL and NEN in 2020.

Results

Flow metering

Partners have surveyed seven different hydrogen refueling station operators to understand their different operating conditions and where in the system their flow meter is situated. This has helped the project's understanding of the suitable maximum permissible error for hydrogen refueling stations. A report of these findings had been written and was sent to the convener of OIML TC8 SC7 to support a revision of OIML R139-1 (which is the current international recommendation for flow metering at the hydrogen refueling station).

Partners received flow meters from commercial manufacturers as in-kind funding which were tested at different temperatures and pressures related to the operational conditions of hydrogen refueling stations (including pressures up to 875 bar). Flow metering calibration protocols were developed using alternative gases to hydrogen (nitrogen, water and oil) to provide calibration laboratories with a safer way to perform traceable calibration of hydrogen flow meters. VSL, METAS and JV will also further work regarding sonic nozzles for hydrogen flow measurement in the new EMPIR project 20IND11 MetHyInfra project.

Primary gravimetric flow metering standards have also been produced and validated as part of this project (Figure 1); these mobile facilities are capable of calibrating flow meters in-situ at hydrogen refueling stations at the extreme operating conditions expected during refueling (700 bar).

Figure 1: The new Primary Standard built by METAS

Four primary standards for refueling at a hydrogen refueling station were developed and tested (by Cesame, METAS, VSL and JV). Some of these standards will be further used in EMPIR project 19ENG04 MetroHyVe 2 but can already be provided to industry.

As a final activity, the project provided a report recommending the development of a primary test bench for performing traceable calibration of hydrogen flow meters at pressures up to 875 bar with target accuracy of 1.5 % and following technical requirements stipulated in OIML R 139-1 and international standard SAE J2601. This report provided a tentative design for the proposed primary calibration test rig with associated uncertainty budget. The facility was expected to cost around €1.4 million. Whilst the facility is of importance to support the metrology community with flow metering, it was suggested that a single NMI working alone would not be able to develop, build and run the rig – it would require collaboration between multiple laboratories.

This objective was successfully achieved.

Hydrogen quality assurance

A literature review was carried out to identify new methods for measuring impurities in hydrogen as required by ISO 14687 Grade D; the last literature review of this kind was performed in 2015 meaning that new methods that had become available over the past five years had not been reported in an available literature review paper of this kind. CEM, AP2E, IFE, NPL, RISE, SINTEF and VSL successfully developed new analytical techniques to measure low level reactive impurities which were previously unavailable to the hydrogen industry. In an effort to ensure the project remained up to date with outside activities, all activities involving development of ISO 14687 methods were updated following the development of a new standard (ISO 21087) published at the end of 2018 which provided guidance on criteria for hydrogen purity measurements when performing analysis according to ISO 14687 Grade D. This new standard (ISO 21087) includes parameters such as limit of detection, accuracy, linearity etc. for each impurity threshold listed in ISO 14687 Grade D. All partners agreed to perform additional work to compare their methods against ISO 21087 and provide validation reports. The new methods developed in the project and by other laboratories outside of the project were reported through reports and peer reviewed papers which are now available to the hydrogen industry. This includes the development of a low cost "all-in-one analyser" developed by RISE in collaboration with AP2E to tackle the impurities from electrolysis; this was done by combining routine Gas Chromatography (GC) methods with Optical Feedback Cavity Enhanced Absorption Spectroscopy (OFCEAS).

A hydrogen impurity enrichment device has been tested for the first time with low level sulphur, and the results have indicated that a palladium-gold membrane (which was expected to be suitable for this technique) was in fact not suitable and led to severe reduction in hydrogen flux. Ten new membranes were prepared (two more than originally specified) and the best performing membrane was successfully used to enrich a hydrogen sample taken from a UK HRS.

A method for filter weighing (during analysis of particles in hydrogen) has also been developed and validated, and a good practice guide on this is available for the hydrogen industry.

Hydrogen mixtures were prepared, and stability tested for the MetroHyVe Offline Comparison which assessed 13 laboratories from around the world (Europe, Asia and USA) in performing hydrogen purity analysis against ISO 14687 Grade D (Figure 2). This comparison was successfully completed and has shown that not all commercial laboratories were able to provide accurate results, with a key mistake being underestimating the uncertainty.

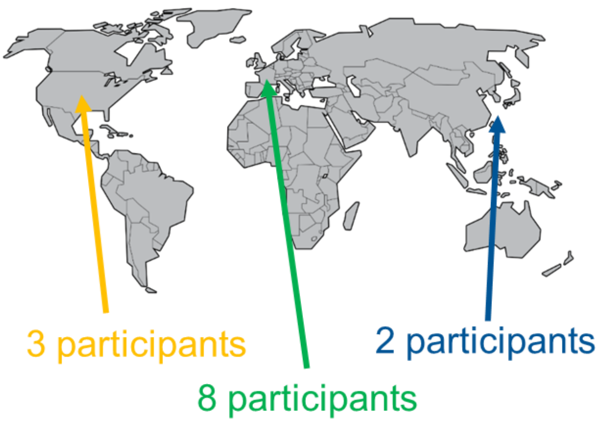

Figure 2: Location of participants of the MetroHyVe Offline Comparison

This objective was successfully achieved.

Hydrogen quality control

Three partners (Shell, CT and AP2E) developed online instruments for measuring key impurities and have completed testing against gas mixtures containing low level hydrogen sulphide, carbon monoxide, oxygen and water in hydrogen which were produced by NPL. The project has received several hygrometers from external collaborators for testing at NPL's humidity facilities. A good practice guide was written by NPL including some important good practice regarding drift of the sensor which can seriously affect accuracy of the device. Currently the hydrogen industry is not aware of this issue, so the good practice guide can make a significant impact. Five commercial online purity analysers covering measurement of H_2S, CO, O_2 and H_2O were tested at NPL; these analysers were provided as in-kind funding and included two analysers from the USA. The tests were completed and the results fed back to the participants. The comparison exercise showed that not all instruments were fit-for-purpose for online monitoring of impurities in hydrogen, but it was promising to see that some were able to provide excellent results. An extensive review of low-cost sensors for hydrogen quality control was written which included testing of a real sensor.

This objective was successfully achieved.

Sampling

Sampling methods have either been developed (as for purging methods at the HRSs) or properly validated as for particulate analysis using filters. Good practice guides were written for these methods, and were demonstrated at two training courses (workshops for hydrogen sampling) hosted by NPL and NEN in 2020. As part of the studies, the stability of impurities in sorbent tubes and gas cylinders were evaluated to ensure the sample would remain representative during transport and while being kept in the laboratory for a long time before actual analysis.

Figure 3: Testing a commercial hydrogen sampling device

This objective was successfully achieved.

Impact

To ensure the project activities remained aligned with stakeholder needs the consortium had built up a stakeholder advisory board of around 50 members; including vehicle manufacturers, gas producers and laboratories. Representatives of key standardisation committees were also included in the stakeholder advisory board, including experts and chair persons. To ensure the project remained relevant to hydrogen industry, the advisory board influenced changes to some activities.

Main dissemination activities included a keynote speech on the project at the World Hydrogen Energy Conference in Brazil (2018), 22 other conference presentations, presentations at standardisation committees including a talk on this project at the plenary meeting for ISO TC 197 Hydrogen Technologies. MetroHyVe held the first workshop on measurement challenges for hydrogen vehicles (in partnership with the Horizon 2020 Cross-Cutting project HYDRAITE), hosting around 80 participants from around the globe, and another two workshops to support industry to perform accurate sampling.

Impact on industrial and other user communities:

The activities and reports produced by the project were regularly disseminated to OIML TC8 SC7, and along with this MetroHyVe partners attended committee meetings to support revision of OIML R139-1 which provides maximum permissible errors for flow metering at HRS. The follow-up EMPIR project 19ENG04 MetroHyVe 2 may consider proposing a revision to OIML R139-1.

The sampling campaign performed in this project proves that there is a certain minimum number of purges that are required to remove air and water contaminants from sampling devices. Tested methods for sampling particulates and gas have been written into reports and good practice guides which will support HRS operators through this process. The impact is significant as HRSs need to be able to sample hydrogen without contaminating it otherwise laboratories will provide test reports showing that their hydrogen fails to meet ISO 14687. Following from MetroHyVe activities, ISO TC 197 have now set up a new working group to focus on sampling methods at hydrogen refuelling stations which is being co-chaired by SINTEF and NPL (partners of this project).

Online instruments have been developed to measure key impurities in hydrogen, and since testing had been carried out at NPL, the project could determine their suitability as hydrogen quality control measures. These devices provided by AP2E, Shell and CT can either be further developed or sold commercially (where data from this project can be used to show instrument performance). Furthermore, in the online comparison two additional instruments were rigorously tested; and results from the comparison can be used to either further develop the instrument or be used to show customers that it performs well. MetroHyVe partners provided additional support to these participants by explaining possible issues with their measurement which was mainly regarding calculation of measurement uncertainty.

The offline comparison robustly assessed commercial hydrogen purity laboratories in their ability to accurately provide hydrogen purity measurements as specified by ISO 14687. In total 13 laboratories from Europe, Asia and USA participated, and the results first of all highlighted that not all laboratories could correctly measure the reference value; in these cases the results were fed back and where required NPL and VSL supported the laboratories by providing additional advice to correct measurements. The activity also impacted the hydrogen quality community by highlighting the importance of running annual schemes such as this one.

An online virtual measurement service hub (via a website) has been created at NPL and is listing laboratories and their hydrogen capabilities. The hub allows end-users to easily find and access these laboratories. The hub will remain open and managed by EMPIR project 19ENG04 MetroHyVe 2.

Impact on the metrology and scientific communities:

Four primary gravimetric standards were built to verify hydrogen flow meters under real conditions using 875 bar hydrogen. These standards can be used across Europe to ensure hydrogen fuel dispensed from stations is calculated accurately in accordance with the requirements of OIML R139-1.

New calibration gas standards were made with improved stability for low level reactive impurities in hydrogen. Gas producers are able to use these to certify their calibration standards for all impurities in ISO 14687 to ensure they are providing traceable values. These new standards are now being advertised and sold by the NMIs as new products. These can already be purchased by research organisations, manufacturers of fuel cells, laboratories, calibration gas providers and universities.

Testing of sorbent tubes and gas vessels for different types of impurities in hydrogen has been completed including an assessment of stability periods. Gas analysis laboratories are able to use the project's report on this subject to select suitable sampling vessels for customers requiring their services. This work will improve the stability of impurities in hydrogen samples.

Impact on relevant standards

ISO 14687 has now been revised based on influence from MetroHyVe partners to remove 'key halogenated compounds' from the standard. This was due to the fact that no methods existed to perform this measurement, which was an activity of the project. Another revision cycle may start in 2021 (to revise Grade D of ISO 14687 which is related to fuel cell hydrogen purity).

ISO 21087 includes an updated review which was performed by NPL and took information directly from the MetroHyVe project regarding new analytical methods.

ISO 19880-8 has yet to be revised, but MetroHyVe partners will ask to include an update on available online purity analysers.

ISO 19880-1 included an annex on sampling, but this part will now be written into an independent standard. SINTEF will head this activity.

Longer-term economic, social and environmental impacts

The long-term goal of this project is to support the introduction of hydrogen vehicles which if replacing conventional petrol cars can help Europe to reach its challenging emission targets.

A low cost all-in-one analyser was developed by RISE in collaboration with AP2E which fulfilled the goal of lowering cost and labour to perform all impurity measurements required for electrolysis. The development of new hydrogen purity methods by the project will help to prevent serious damage to fuel cell vehicles by allowing the hydrogen industry to perform all hydrogen purity measurements as required by ISO 14687 Grade D. Such damage would be costly for the automotive manufacturers to replace and therefore its prevention will promote the introduction and manufacture of hydrogen fuel cell vehicles.

The implementation of online hydrogen purity analysers developed in this project will in the long-term reduce the need for contracting regular hydrogen purity analysis by a commercial laboratory with an important cost reduction in quality assurance of hydrogen. New players entering the hydrogen industry will be able to use the new reports and good practice guides to learn the importance of laboratory accreditation and how to prove competency through interlaboratory comparisons. Both developments will support the use of hydrogen as a fuel for fuel cell vehicles and will also provide suppliers and end-users with confidence in the quality of their hydrogen fuel.

List of publications

Measurement challenges for hydrogen vehicles, A. Murugan, M. de Huu, T. Bacquart, J. van Wijk, K. Arrhenius, I. te Ronde and D. Hemfrey, International Journal of Hydrogen Energy, Volume 44, Issue 35, July 2019, Pages 19326-19333. https://doi.org/10.1016/j.ijhydene.2019.03.190

Hydrogen refuelling station calibration with a traceable gravimetric standard, R. Maury, C. Auclercq, C. Devilliers, M. de Huu, O. Büker and M. MacDonald, Flow Measurement and Instrumentation, Volume 74, August 2020. https://doi.org/10.1016/j.flowmeasinst.2020.101743

Design of gravimetric primary standards for field-testing of hydrogen refuelling stations, M. De Huu, M. Tschannen, H. Bissig, P. Stadelmann, O. Büker, M. MacDonald, R. Maury, P. T. Neuvonen, H. T. Petter and K.Rasmussen, Flow Measurement and Instrumentation, Volume 73, June 2020. https://doi.org/10.1016/j.flowmeasinst.2020.101747

Investigations on pressure dependence of Coriolis Mass Flow Meters used at Hydrogen Refuelling Stations, O. Büker, K. Stolt, M. de Huu, M. MacDonald, R. Maury, Flow Measurement and Instrumentation, Volume 76, December 2020. https://doi.org/10.1016/j.flowmeasinst.2020.101815

Hydrogen Purity Analysis: Suitability of Sorbent Tubes for Trapping Hydrocarbons, Halogenated Hydrocarbons and Sulphur Compounds, Karine Arrhenius, Haleh Bohlen, Oliver Büker, Iris de Krom, Dita Heikens and Janneke van Wijk, Applied Science 2020, 10 (1), 120. https://doi.org/10.3390/app10010120

Development and evaluation of a novel analyser for ISO14687 hydrogen purity analysis, Karine Arrhenius, Oliver Büker, Andreas Fischer, Stefan Persijn and Niamh D Moore, Measurement Science and Technology, Volume 31, Number 7. https://doi.org/10.1088/1361-6501/ab7cf3

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/.

Project start date and duration:	June 1st 2017, 39 months	
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Internal Funded Partners: 1 NPL, United Kingdom 2 CEM, Spain 3 Cesame, France 4 FORCE, Denmark 5 JV, Norway 6 NEL, United Kingdom 7 RISE, Sweden 8 VSL, Netherlands	External Funded Partners: 9 Air Liquide, France 10 AP2E, France 11 CT, United Kingdom 12 FHA, Spain 13 IFE, Norway 14 ITM, United Kingdom 15 Linde, Germany 16 NEN, Netherlands 17 SINTEF, Norway	Unfunded Partners: 18 Empa, Switzerland 19 METAS, Switzerland 20 Shell, Netherlands
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