Publishable Summary for 15NRM03 HYDROGEN
Metrology for sustainable hydrogen energy applications

Overview

The EU Energy Strategy for transport and the dedicated European policy objectives encourage the wide use of hydrogen for the transport sector. The fast evolution of the hydrogen sector pushes to reconsider the international normative documents. The project addressed the standardisation needs in the hydrogen-energy sector by supplementing and feeding four ISO standards in development or in revision through metrology research studies: ISO 14687, ISO 16111, ISO 19880-8 and ISO 21087. This project provided to the standardisation bodies the guarantee of validated techniques and traceable analysis measurements at the highest accuracy levels.

Need

The use of hydrogen is a promising solution to solve the conflict between the growing need for energy, the depletion of fossil fuels, the greenhouse effect and the climate change challenge. The ongoing technical and scientific developments in hydrogen quality control, hydrogen transportation application, distribution, production and storage of hydrogen require constant reassessment of the regulatory documents.

The European Directive on the deployment of alternative fuels infrastructure 2014/94/EU stated that the hydrogen purity dispensed at hydrogen refuelling stations should comply with the technical specifications included in ISO 14687-2. The rapid progress of the fuel cell electric vehicles required revising this standard towards less constraining detection limits and simultaneously ensuring a low impact risk of impurities on fuel cells (ISO 19880-8). Validated analytical techniques, used to measure each impurity in hydrogen according to these specifications, needed in turn to be standardised in a new standard including validated protocols. There was a need to comply both with accurate analytical measurements at low levels of concentration respecting ISO 14687 specifications with validated techniques. In addition, for cost purpose, the number of required analyses had to be reduced using a multi-component analyser.

The normative framework related to ISO 16111 for hydrogen absorbed in reversible metal hydride was improved in the Working Group 25 within ISO/TC 197 by broadening the scope of the former version of the standard published in 2008 to larger hydrogen volumes through traceable methods for the measurement of the amount of hydrogen absorbed in the metal hydrides. There was a need to provide accurate measurements by validated methods (mass methods or flowmeters). One objective of the project was to contribute to the improvement of the hydrogen mass measurement method and its validation.

Objectives

This project outputs aimed at feeding the revisions and development of four ISO standards dealing with hydrogen characteristics used for transportation and storage.

The specific technical objectives of the project were to:

1. Develop hydrogen quality specifications for fuel cell vehicles, including tolerance levels for impurities in hydrogen and limits for the degradation of fuel cell performance as per ISO 14687-2 'Hydrogen fuel - Product specification – Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles 2012'. This included recommendations on maximum concentration of individual compounds based on the new fuel cell degradation studies and on the probability of presence.
2. Propose optimised analytical protocols (including fit-for-purpose analytical methods) and assess an analyser that would enable the implementation of ISO 14687-2. The multicomponent analyser should have optimised sampling analysis and met the required detection limits as per business plans

ISO/TC 197 “Hydrogen technologies” 2005-11-07 and CEN/TC 268 “Cryogenic vessels and specific hydrogen technologies applications” 2014-04-04.

3. Develop and validate traceable methods for measuring the hydrogen mass absorbed in storage tanks (hydrides AB, AB2 and AB5), with reference to ISO 16111 “Developing transportable gas storage devices - Hydrogen absorbed in reversible metal hydride”.
4. Contribute to the standards development work of key European and International Standards Developing Organisations ensuring that the outputs of the project were aligned with their needs, communicated quickly to those developing the standards and to those who use them, and in a form that could be incorporated into the standards at the earliest opportunity.

Progress beyond the state of the art

Development of hydrogen quality specifications for fuel cell vehicles and input proposal for ISO 14687-2 and 19880-8 standards

The project drew up a risk assessment matrix of impurities taking into consideration the probability of presence of hydrogen impurities regarding the three main hydrogen production processes through traceable measurements on 27 hydrogen samples from production sites all around Europe and their impact in terms of toxicity on a new generation of fuel cells. Outputs have been reported to standardisation working groups for ISO 14687 and ISO 19880-8 standards dealing with hydrogen quality control at fuelling stations.

Development of optimised analytical methods for hydrogen impurity analysis

The analysis techniques listed in the newly published ISO 21087 standard (June 2019) to measure hydrogen impurities are costly and time consuming for the actual increased end-use applications of hydrogen and the ongoing improvement of fuel cells for mobile applications.

Multi-component analysers were a promising way to reduce the number of analyses for hydrogen quality. The proper validation of these instruments was missing. Considering the analytical methods proposed at the project started, there was a need to compare and to establish a roadmap for validation of the proposed methods. External laboratories can now validate instruments using established procedures and certified reference materials. Performance technical characteristics were studied and speciation methods for multispecies families have been developed as total species determination was a real analytical challenge for metrology consideration.

Development of traceable methods for hydrogen mass measurements absorbed in metal hydrides: proposal for a revised ISO 16111 standard

There was a lack of standardised and traceable methods for the measurement of the amount of hydrogen absorbed in metal hydrides, particularly for the increasing absorption capabilities of metal hydrides. A consistent method has been recommended for traceable mass measurements of hydrogen absorbed in hydride tanks.

Results

When the project started, standardisation activities supported the revision of standards in hydrogen fuel applications: merging of the ISO 14687 standards family (and jointly to revise ISO 14687-2 for hydrogen specifications) and revision of ISO 16111 to widen its application. The resulting ISO 14687 standard is in advanced stage of the revision process at ISO/TC 197 (DIS stage stands for Draft International Standard is the antepenultimate step before publication) and ISO 16111 is published since August 2018. During the timeframe of the project, the analytical methods enabling the assessment of the molar concentrations of impurities in hydrogen and previously suggested in an informative annex of ISO 14687-2 were removed during revision of ISO 14687-2 and development of ISO 14687 in order to be treated in a new standard ISO 21087 “Hydrogen fuel – Analytical methods – Proton exchange membrane (PEM) fuel cell applications for road vehicles” that is now published since June 2019. The project aimed at evaluating the performance of analytical methods, existing and under development, to perform hydrogen purity testing (number of parameters covered, uncertainties, risk for interferences and robustness) with a high level of confidence. Additionally, and during the same time, ISO 19880-8 “Gaseous Hydrogen—Fuelling stations—Part 8: Fuel Quality Control” has been developed (DIS stage for upcoming publication) to specify the protocol for ensuring the quality of the gaseous hydrogen quality at fuelling stations for PEM fuel cells vehicles.

The four standards are under the responsibility of ISO/TC 197 “Hydrogen Technologies” (jointly with ISO/TC 158 “Gas Analysis” for ISO 21087. Besides the ongoing standardisation activities supporting the development of these four ISO standards, the scientific, technical and metrological work performed in the project is highly relevant at the standardisation levels.

Development of hydrogen quality specifications for fuel cell vehicles and risk analysis of impurities to manage and limit the degradation of fuel cell performance

The probability of impurities (ammonia, Ar, CO, CO_2, formaldehyde, formic acid, H_2O, He, N_2, O_2, total halogenated compounds, total hydrocarbons compounds, total sulphur compounds) presence in hydrogen for fuel cells was investigated by process experts for steam methane reforming (SMR), PEM water electrolysis and chlor-alkali membrane electrolysis processes. The number of real hydrogen samples analysed at SMR and PEM water electrolysis plants and at an HRS for the chlor-alkali membrane electrolysis sample exceeded the number initially planned as 27 samples have been treated (21 were planned). The thirteen gaseous impurities listed in ISO 14687 have been analysed. It was the largest sampling analytical campaign for metrology purposes performed in Europe at sixteen different locations. It was observed from the results that the hydrogen quality was compliant with ISO 14687 for the application in fuel cell electrical vehicles. Furthermore, the probability of presence of the thirteen gaseous impurities has been investigated for the main hydrogen production processes (steam methane reforming – SMR - with pressure swing adsorption and water proton exchange membrane – PEM - electrolysis process with temperature swing adsorption and chlor-alkali membrane electrolysis process). During the project, a set of evidence to support expert assessment about hydrogen quality at the production outlet has been provided.

The study exposed that no contaminant above ISO 14687 thresholds in hydrogen from SMR or PEM water electrolysis was measured but that sampling could lead to contamination. The study investigated the impact of temperature swing adsorption for PEM water electrolyser and identified the key contaminant to be monitored.

The impact of 2 ppm of NH_3, 0.2 ppm of HCl and 0.2 ppm of 1,2,3,4-tetrachloro-1,1,2,3,4,4-hexafluorobutane ($C_4Cl_4F_6$) on a FC performance under stationary and dynamic test protocol of overall ~900 h duration was investigated over ~ 900 h using stationary and dynamic test protocols. The results have been compared to the reference cell tested in pure hydrogen. At the beginning, it was previously considered that their impact was poorly investigated in the literature especially over long term and under driving cycling conditions. Ammonia NH_3 is a potential poisoning of ionomer at a fuel cell stack and only a few data concerning low concentrations below 5 μmol/mol are available. Hydrogen chloride HCl could be absorbed on Pt enhancing its dissolution. It was known that production of chloride ions issued from the presence of HCl was responsible for inhibiting the oxygen reduction reaction. $C_4Cl_4F_6$ is a compound that has been found in several hydrogen samples and no literature data on its impact was found. It can also be adsorbed on Pt surface and partially decomposed with the formation of HCl and HF in fuel cell test conditions. NH_3 at 2 μmol/mol, HCl at 0.2 μmol/mol and $C_4Cl_4F_6$at 0.2 μmol/mol have been prepared by NMIs partners of the project. All the impurities induced reversible and irreversible cell performance losses during the electrochemical test, which were considerably larger compared to that ones for baseline test in pure H_2. Observing the various cleaning techniques and their importance, was also discussed. The performance decay for the cells tested with the pollutants was partially recovered via electrochemical characterisation and cell decontamination in neat H_2 applied after each phase of the test. $C_4Cl_4F_6$ exposure resulted in the highest reversible and irrecoverable FC performance losses and it was admitted that the actual threshold for ammonia can be relaxed to 0.5 μmol/mol. The announced total halogenated compounds specification of 0.05 μmol/mol seemed to be reasonable.

A risk assessment was proposed taking into consideration the severity level of impurity from literature and the results of the project. It has been integrated to the definition of occurrence declared in the ISO/DIS 19880-8 standard. Question was raised to add both severity classes in the risk assessment matrix as well as mid-specification higher than ISO thresholds with lowest severity classes.

Development of optimised analytical methods for hydrogen impurity analysis

While ensuring the hydrogen specifications, analytical and sampling methods have been detailed in ISO 21087 standard “Hydrogen fuel – Analytical methods – Proton exchange membrane (PEM) fuel cell applications for road vehicles” published in November 2018. This new standard was elaborated under the responsibility of the

Joint ISO/TC 158 – ISO/TC 197 working group 7 “Hydrogen fuel analytical standard” and now includes suggested and optimised validated analytical methods to meet the ISO 14687 specifications for hydrogen impurities measurements. To support the use of multi-component analysers and their flexibility to meet the clients’ specifications and needs, the project aimed at controlling cross-check of the analytical methods for measuring all the 13 hydrogen impurities of the ISO/DIS 14687standard with regards to the performance characteristics of the methods. The performance characteristics to assess for validation are the working range, limit of detection, selectivity, linearity, robustness, trueness, precision and limit of quantification. Volume was needed as well as pressure and the nature of the sampling vessels.

The actual analytical methods for the full implementation of the ISO 14687 standard were referenced thanks to contacts made with off-line analyser manufacturers. Thus, four multi-component analysers and their specifications have been considered: CRDS (cavity ring-down spectroscopy), FTIR (Fourier Transform InfraRed spectroscopy), OFCEAS(Optical Feedback Cavity Enhanced Absorption Spectroscopy) and BTL (Broadly Tunable Laser) methods. Apart of this review, new speciation methods for sulphur, halogenated and hydrocarbon species were developed and validated by three NMIs partners of the project.

Information was cross-checked after discussion with manufacturers, available data in the literature about the existing methods and feedback from users at laboratories. In addition, potential harmful compounds have been looking for in real hydrogen samples and not yet regulated in ISO 14687. It resulted in the absence of such compounds performing analyses with a VOC screening method at ppb levels.

In conclusion, it was pointed out that there was a need for complete validation of the proposed methods as required in ISO 21087 by external laboratories as NMIs with certified reference materials to validate these methods.

Traceable methods for hydrogen mass measurements absorbed in metal hydrides

For the determination of the best fitting system for hydrogen mass measurements, two hydride tanks have been made, filled with AB5 hydride type and AB hydride type and sent to research laboratories for testing.

Charge/discharge cycles have been performed with the metal hydride tanks AB5 received. It was highlighted that the input parameters and experimental conditions as temperature, pressure, flows considering the mass and nature of metal hydride were of prime importance for optimised charging and discharging hydrogen in metal hydride as several unexpected findings have been discovered during the measurements (e.g. over-flow on mass flow meter in case a system with non-regulating valves used, deviation of mass flow meter measurement depending on the line pressure and pressure difference). A good fitting curve on mass flow calibration error was needed to fix biases observed for mass flow meters used. It was recommended also a purity of hydrogen at a higher level than 4.5 (99.995%) as hydrogen can degrade the hydride.

The behaviour of the AB-type tank was observed to be similar to the AB5-type tank, but it was loaded with a higher maximal pressure. The properties differed regarding flow kinetic that was lower for AB-type and a degradation of the AB-hydride during the 20 first cycles was observed. Comparison of AB-type tanks could not be performed as the absorption in the hydride was not detectable at one partner’s laboratory.

Meanwhile, work performed in this task led to conclusions about the best-practise test facility design as the use of pressure controllers, well-placed as regard to needle-valves and use of one or several flow meters adequately calibrated. Piping systems with needles valves and mass flow controllers are been compared, both solutions required the mass flowmeter to work under different pressures for loading and unloading phases: approximately at the source pressure for loading and approximately at the outlet pressure (atmospheric pressure) for unloading. Both solutions required a calibration of the mass flowmeter at two pressures.

Needle valves use was guided by the choice to avoid mass flow controller use but this solution included a more complicated gas circuit with more components. It suffered from a pronounced "saturation" effect, which made the mass flowmeter to work in a saturated state leading to unexpected and uncontrolled measurement deviation.

Impact

Continuous activities have been undertaken to support the uptake and use of the project’s outputs to the stakeholder hydrogen community (industrial and regulatory organisations). The consortium has given a substantial number of technical and general presentations of the project’s outputs at international events.

Impact on industrial and other user communities

The industrial and user communities of hydrogen were the targeted beneficiaries of the project outputs. The uptake of the expected knowledge and methods from the project had a direct effect on the hydrogen industrial community: producers, consumers, distributors and manufacturers of analytical gas analysers and storage tanks. Follow-on collaborations with companies or laboratories not involved in the project as Shell, ITM power, SINTEF, LINDE and CNH2 enabled the achievement of objectives in terms of impurities measurements. AP2E Company, a collaborator of the project, promoted a project output for commercial use towards prospective customers. Moreover, AP2E organised a round-table debate at the Industrial Analysis Exhibition in February 2018 with project's partners questioning the adequate gas analysis methods to control the purity of the hydrogen in order to support the market development of fuel cells. Two articles were published in professional journals in 2018 promoting the project dealing with hydrogen quality. More than four publications have been published in *Gasworld*, *Mesures, Hydrogen Platform,* on the *hydrogen purity* Wikipedia page and on a partner's general website.

Industrial stakeholders as fuel cells manufacturers, gas analyser manufacturer or hydrogen producers reiterated their interest to be member of the stakeholder advisory board and to be informed of the expected outputs of the project. A wide variety of international industries, automotive and spatial industries, hydrogen producers, hydrogen storage and distribution companies, research centres, gas analysers manufacturers and investment banks attended the international workshop of the *Hydrogen* project held at the Air Liquide R&D Centre "Campus Innovation Paris". The hydrogen project was identified at the new European Metrology Network on Energy Gases launched in 2019.

Impact on the metrology and scientific communities

This project was the first metrology European project related to hydrogen within the EMPIR Programme. The wider impact was that metrology for hydrogen purposes in industry, standardisation or other user communities became the guarantee for validated techniques and traceable measurements in any hydrogen topic.

Results have been presented at 23 international conferences and six papers have been published or submitted to dedicated scientific journals: one paper has been published in *Measurement Science and Technology* following the International Congress of Metrology 2017, another one was an Open-Access publication in the *International Journal of Hydrogen Energy* (2018), two papers were included in proceedings books of conferences (Iberconappice and ISFFM) and two open-access papers have been submitted respectively to the *Journal of Power Sources* and *International Journal of Hydrogen Energy*.

The website of the project was regularly updated at http://projects.lne.eu/jrp-hydrogen/ with news items or information regarding events or conference attendance.

Impact on relevant standards

Through the dissemination of the project outputs at the CEN and ISO level, answering cross-cutting issues through metrology studies provided new knowledge for the improvement of standards. The exploitation of results directly impacted the standardisation works following the close interactions between partners of the project and their commitment in the working groups of ISO/TC 197. Outputs of the project impacted the standardisation works in the relevant working groups of the International and European regulatory bodies: at ISO/TC 197 / WG 28 for hydrogen quality control, ISO/TC 197/WG 27 for hydrogen fuel quality and ISO/TC 197 – ISO/TC 158 / JWG7 for hydrogen fuel analytical methods. All deliverables of the project were sent to decision makers at working groups of ISO/TC 197. In addition, regular information and work-in-progress have been relayed at national mirror ISO/TC 197 committee meetings.

Longer-term economic, social and environmental impacts

Zero-emission vehicles use as fuel cells electric vehicles powered with hydrogen reduces the pollution levels in urban areas. In addition, if this hydrogen is produced from renewable energy sources, it is the energy solution to mitigate the impacts of global climate change and the alternative renewable energy to fossil fuels. The project results with a global aim to enhance hydrogen use for mobility and storage will, in its entirety, have an environmental impact on hydrogen vehicles use through the consideration at standardisation ISO/TC 197.

It leads also to a potential effect on developing countries' populations that are encouraged for many years to support International and European standards to promote hydrogen use as an energy fuel and to decrease their dependency of fossil fuels.

The scientific result related to the impact tests of three key impurities on fuel cell performance led to suggest relaxing ammonia specification for further consideration at ISO/TC 197/ WG 27. If considered for future revision of ISO 14687, this will have a wider economically impact both the fuel cells manufacturers and hydrogen producers and consequently the gas analysers manufacturers to adopt less stringent but also validated technique for ammonia.

Moreover, achieving durable cost reduction of hydrogen technologies associated with its production, transport and utilisation is a matter somehow of defining hydrogen characteristics to ensure access to a product of quality. The ability to easily control hydrogen purity was an important issue not only for fuel cells manufacturers that ensured the reliability and lifespan of their products by the ISO 19880-8 application, but also for users who have now the guarantee of the performance of fuel cells. By developing the risk assessment matrix of impurities taking into consideration the probability of presence of hydrogen impurities and their impact in terms of toxicity, the reliability and lifespan of fuel cells will be guaranteed through the ISO 19880-8 application.

In parallel, the project aimed at assessing the status of the analytical methods available in the market for hydrogen impurities accurate measurements in terms of performance characteristics and validation data, at assessing multi-component analysers (FTIR, OFCEAS, CRDS, BLT) through discussion with providers, end-users and literature study to reduce the number of analyses totally required and at developing and validating three speciation methods for S-compounds, halogenated (HCl) and hydrocarbons. The outputs linked to this last objective have been transferred to be a documentary support at ISO/TC 197 - ISO/TC 158 JWG 7 (hydrogen fuel analytical methods) to ensure hydrogen quality for fuel cell applications for road vehicles. He document will help gas analysers' manufacturers to propose fit-for purpose validated analytical methods enabling the implementation of ISO 14687 based on their clients' requirements for characteristics performances (selectivity, trueness, precision and working range), costs and possibly other specific requirements as response time, volume the gas needed or the possibility to work with different gas matrices.

At the same time, hydrogen use as a safe energy must be accepted by the public and education is needed to overcome the feeling of fear that remains mainly when thinking of any hydrogen application. The international workshop held at Campus Innovation Paris (Air Liquide R&D Centre) where training courses have been given to people coming from various hydrogen interests bases. It deeply contributed to the social acceptance of hydrogen as broadly use energy vector. Safe storage of hydrogen in metal hydrides and newest recommendations released within the project is one of the ways to change mindsets.

List of publications

- Probability of occurrence of ISO 14687-2 impurities in hydrogen:principles and examples from steam methane reforming and electrolysis(water and chlor-alkali) production processes model,T. Bacquart, A. Murugan, M. Carré, B. Gozlan, F. Auprêtre, F. Haloua, T.A.Aarhaug, *International Journal of Hydrogen Energy*, Vol. 43 (2018) pp. 11872-11883, https://doi.org/10.1016/j.ijhydene.2018.03.084

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<tr><td colspan="2">Project start date and duration:</td><td>1 June 2016, 36 months</td></tr>
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<tr><td>Internal Funded Partners:
1. LNE, France
2. CEM, Spain
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4. RISE, Sweden
5. VSL, Netherlands</td><td>External Funded Partners:
6. AH2GEN, France
7. Air Liquide, France
8. CEA, France
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