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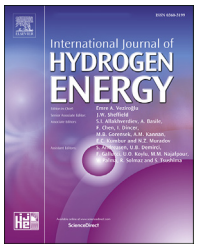

Measurement challenges for hydrogen vehicles

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ABSTRACT

Uptake of hydrogen vehicles is an ideal solution for countries that face challenging targets for carbon dioxide reduction. The advantage of hydrogen fuel cell electric vehicles is that they behave in a very similar way to petrol engines yet they do not emit any carbon containing products during operation. The hydrogen industry currently faces the dilemma that they must meet certain measurement requirements (set by European legislation) but cannot do so due to a lack of available methods and standards. This paper outlines the four biggest measurement challenges that are faced by the hydrogen industry including flow metering, quality assurance, quality control and sampling.

Introduction

Many countries worldwide are encouraging the introduction of hydrogen vehicles onto their roads, with significant efforts being made in Japan, USA and Europe. Hydrogen vehicles provide the benefits expected of an electric vehicle by allowing no carbon-containing gases to be produced in the exhaust, but their performance also remains very similar to conventional vehicles with regards to range and speed. The shorter fuelling time for a hydrogen vehicle is a significant improvement on battery electric vehicles; a complete refuel can be undertaken within three to 5 min [1]. It should be noted that the method for refuelling a hydrogen vehicle is very similar to that for a petrol or diesel vehicle. Refuelling is performed at dedicated refuelling stations using a pump, and so is a very intuitive process for those familiar with petrol and diesel vehicles.

Whilst many countries are supporting the use of hydrogen cars to meet stringent climate change targets, the introduction will not be quick and easy. Hydrogen vehicles cannot operate without a proper hydrogen refuelling infrastructure in place, and similarly hydrogen refuelling stations cannot realistically open without sufficient demand. This conundrum is often referred to as the 'chicken and egg' dilemma in the industry. However, as hydrogen vehicles already have good

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support from national governments and industry, it is clear that the hydrogen economy will grow at a fast pace over the next few decades. There are already over 100 fully functioning hydrogen refuelling stations across Europe [2].

There are however significant problems which arise from specific measurement challenges. These include, for example, a refuelling station's inability to quantify the amount of hydrogen dispensed into a hydrogen vehicle during refuelling to a sufficient degree of accuracy. Without addressing this issue the customer cannot be charged correctly, which has a knock on effect on the station owner, hydrogen producers and Governments through potential lost tax revenue. For other types of measurement requirements, such as hydrogen quality, stations will need to carry out very challenging purity analysis to ensure there are no impurities in the hydrogen that can damage the fuel cell (even 4 nmol mol^{-1} of hydrogen sulphide is a dangerous level) [3]. The consequences of impure hydrogen could be costly, not just in terms of damage to the fuel cell and vehicle performance, but in terms of confidence in the hydrogen refuelling infrastructure at this very early stage. Without certainty in these measurements development of this infrastructure could slow down or stall.

This paper identifies four specific measurement challenges that arise from the introduction of hydrogen vehicles with a focus on European requirements: flow metering, quality assurance, quality control and sampling. For each measurement the requirements set by regulations and standards that produce the challenge are discussed, followed by a deeper discussion on the challenges themselves.

Flow metering

Requirements

As is currently the case with fuel dispensers providing petrol, diesel or compressed natural gas (CNG) to conventional vehicles, the amount of fuel dispensed must be measured so that the customer can be charged the correct amount following refuelling. The ability to quantify the amount of liquid fuel dispensed into motor vehicles is so routine that International Organisation of Legal Metrology (OIML) wrote International Recommendation OIML R117-1 [4] that gives an accuracy class of 0.5% for such dispensing systems (except for LPG, 1% in that case). It is also customary to give the amount of delivered fuel in litres.

Hydrogen refuelling stations look and operate in a very similar way to petrol stations, the only difference being that the delivered amount is presented in kg. The fuelling protocol and process limits are detailed in the SAE J2601: Fuelling protocols for light duty gaseous hydrogen surface vehicles. The end-user drives into an allocated bay, fuels the vehicle and drives off after either paying directly at the dispenser or at a cashier. As is the case for petrol stations, in order for customers to be charged correctly, the quantity of fuel taken into the vehicle must be known. Hydrogen stations use a mass flow meter to perform this measurement.

OIML TC8 SC7 Gas Metering have written an international recommendation OIML R 139-1 [5] which details the metrological and technical requirements for compressed gaseous fuel measuring systems for vehicles (including flow meters used in compressed gas standards). As stated in the scope of the document, the contents apply to hydrogen as well as compressed natural gas, biogas and other types of compressed gaseous fuels. In this recommendation, the maximum permissible error is set at 1% for the measured quantity of the meter and 1.5% of the measured quantity for the entire system. This applies to all possible conditions of temperature, pressure and flow rate that could be feasible during operation.

Whereas conventional fuel dispensers (such as petrol) may be able to meet these targets, for hydrogen dispensers it is not currently possible (as will be discussed in Section Challenges). Therefore a new revision to this standard is in progress where experts from the hydrogen industry and metrology community will work together to set fit-for-purpose accuracy limits. At an OIML technical committee meeting in 2017, specific accuracy classes for hydrogen were proposed and a vote took place in 2018. A preferred accuracy class leading to a maximum permissible error of 2% for the complete measuring system at type evaluation or verification and 1.5% for the flow meter were envisioned, though national authorities may decide to require a less challenging accuracy class. However, much work is required by National Metrology Institutes (NMIs), measurement laboratories and instrument manufacturers to reach these challenging accuracies.

Challenges

The hydrogen in a station can be supplied at pressures as high as 875 bar

No traceable capabilities currently exist in laboratories for calibrating flow meters used in hydrogen refuelling stations at nominal working pressure (NWP) of 700 bar with hydrogen under similar pressure and temperature conditions. In addition to the technical challenges, such a high pressure of hydrogen is very hazardous to work with and most laboratories would not be equipped from a health and safety point of view to handle it. Currently, there are only very limited capabilities for calibrating flow meters that operate at high pressures of hydrogen.

The temperature of the hydrogen can fluctuate between -40 °C and 85 °C

Hydrogen delivered to the vehicle is most often cooled down to −40 °C before entering the vehicle. This allows for a higher pressure ramp rate and shorter fuelling time. The flow meter can either be positioned before or after the heat exchanger, meaning that it measures hydrogen mass flow at a low but almost constant temperature or it measures hydrogen mass flow at an increasing temperature ranging from −40 °C up to 85 °C during refuelling due to compression and Joule-Thompson heating. The influence of fluid temperature on flow meter reading should be investigated to ensure the flow measurement is accurate.

There may be unknown losses of hydrogen

After refuelling, the nozzle must be removed from the vehicle but before this can be performed the line must be depressurised. As the hydrogen could be at high pressures of above 700 bar, the process must allow venting to be carried out away from the customer. However, this procedure may provide some uncertainty to the flow calculation as it would be included in the calculation made by the flow meter, but should not be included

in the costing. A proper method on estimating these venting losses needs to be developed and its contribution to error.

There are currently no primary standards for calibrating flow meters at hydrogen refuelling stations

A metrological framework needs to be developed for testing and calibrating hydrogen flow meters up to 875 bar. Moreover, field test standards based on gravimetric systems suited for measuring hydrogen flow under changing conditions need to be developed for testing and calibrating hydrogen flow meters in the field up to 875 bar. This would allow the establishment of a legal metrological control system for hydrogen dispensers which is currently lacking in many countries and will provide a method to validate these refuelling stations against standards and regulations. Among NMIs, only the National Institute of Standard and Technology (NIST) in the USA has developed a field testing standard for verifying hydrogen refuelling stations but only up to 350 bar [6].

Quality assurance

Requirements

There are two ways hydrogen fuel can be used to power cars. The hydrogen can be burned directly in an internal combustion engine, however this process is not very efficient [7]. Therefore, vehicle manufacturers have steered towards fuel cell electric vehicles (FCEVs) which are efficient but require very high purity hydrogen. The majority of hydrogen worldwide is currently still produced by the steam methane reforming process which uses high temperature chemical reactions to convert natural gas to pure hydrogen. Electrolysis, an alternative method, utilises electricity to split water into hydrogen and oxygen. If the electricity used for this process is derived from solar or wind power, the entire production cycle can be completely free of carbon dioxide.

FCEVs, like any conventional vehicle, require a specific quality of fuel to benefit from the best performance of the system and to avoid technical issues. Based on FCEV and fuel cell manufacturer's requirements and hydrogen sector capability, International Standards on hydrogen quality for FCEVs were prepared at international level (ISO 14687-2 [8]), European level (EN 17124 [9]) and North American level (SAE J2719 [10]). ISO 14687-2 is the standard that is recognised globally as a guide for hydrogen purity, but in Europe it will be mandatory to follow the technical specifications contained within Table 1 as the European Directive on the deployment of an alternative fuels infrastructure [11] states that "the hydrogen purity dispensed by hydrogen refuelling points shall comply with the technical specifications included in the ISO 14687-2 standard" by 18 November 2017. The purity specification for hydrogen supplied to fuel cell vehicles includes thresholds for 13 gaseous impurities and a maximum particulate concentration of 1 mg kg^{-1}.

Table 1 – Hydrogen purity requirements for gaseous impurities in fuel cell electric vehicles (ISO 14687-2).

Impurity	Amount fraction/μmol mol^{-1}
Helium	300
Nitrogen	100
Argon	100
Water	5
Oxygen	5
Carbon dioxide	2
Total hydrocarbon	2
Formic acid	0.2
Carbon monoxide	0.2
Ammonia	0.1
Total halogenated	0.05
Formaldehyde	0.01
Total sulphur	0.004

Hydrogen for FCEVs can be produced by several production processes involving a complete different feedstock, operations and constrains. Different impurities may be present in the final hydrogen delivered to the FCEV and the impurity in question would depend on the process used; for example it would be more likely for small amounts of methane to be present in hydrogen made by steam methane reforming compared to electrolysis.

Due to the stringent regulations and technical challenges (sensitivity of the fuel cells to degradation), in addition to the varying probability of impurities that can be found in different hydrogen production processes, it is crucial to ensure hydrogen provided to FCEVs undergoes quality assurance.

Challenges

Limitations of commercially available analysers

As shown in Table 1, analytical laboratories must be capable of measuring the impurities accurately at very low levels (for example total sulphur at 4 nmol mol^{-1}) [3]. Several recent analytical studies [12–14] review the existing analytical methods available to comply with ISO 14687-2. A variety of gas chromatography or spectroscopy methods that allow these detection limits to be reached may be available even if evidence of method validation in each case is not always available. However to enable measurement of all required impurities at the specified levels several challenges currently faced by analytical laboratories can be identified covering cost, lead time, sample size, accuracy and method validation:

Cost of analysis: to perform the complete analysis of hydrogen according to ISO 14687-2, gas analysis laboratories would need to purchase several state-of-the-art instruments which raise a capital expenditure of around €500,000 [15]. A method to pre-concentrate impurities in hydrogen samples can facilitate the required measurements as it would allow more routine analysers such as gas chromatography with mass spectrometry (GC-MS) to be used to measure most of the analytes. Lowering the number of analysers required for hydrogen purity testing reduces capital cost, turnaround times and volume of sample required. The National Physical Laboratory (UK) have developed a high accuracy Hydrogen Impurity Enrichment Device [16] that can concentrate impurities in hydrogen to high levels (the enrichment factor is calculated by monitoring the amount fraction of a 'tracer' compound added to the hydrogen). Whilst the device was proven to work in the laboratory to enrich hydrogen samples containing nitrogen, methane and carbon monoxide, further work is required to perform similar tests with highly reactive compounds such as hydrogen sulphide and other sulphur-based impurities.

Lead time and sample size: Use of all of these analysers could lead to issues around volume of sample required, particularly if instruments requiring high flow rates such as spectrometers are used. Utilising a high number of analysers can also lead to long turnaround times which would not be of benefit to the hydrogen refuelling stations who would require results as soon as possible to limit damage to customer vehicles. Therefore further work is required to minimise the number of analysers required to perform the full analysis and where possible to minimise gas sample required for the analysis (as this may be limited depending on how much gas can fit into the sampling vessel). The ideal gas analysis system would balance cost, accuracy and should be operator-friendly with automation options to follow the quick expansion of hydrogen networks in Europe and worldwide.

Accuracy and method validation: Currently the methods for performing hydrogen purity analysis rely on mainly gas chromatography, ion chromatography and spectroscopy [12]. However, there is still a lack of validated methods for measuring low level formaldehyde, formic acid, halogenated compounds, sulphur compounds and ammonia in hydrogen. Additionally, to ensure harmonisation between Europe, Asia and the USA the various Japanese (JIS) and American (ASTM) test methods for hydrogen purity analysis must be compared with European methods to assess any bias between these standards and European laboratory capability.

Stability of calibration gas standards

In order for measurements to be accurate they must be performed against traceable calibration gas standards. However calibration gas standards are not readily available for most of the measurements required when performing ISO 14687-2 analysis which is primarily due to the instability of low level compounds in hydrogen. For example, it is not possible to produce a stable calibration gas standard containing 4 nmol mol^{-1} of sulphur compounds in hydrogen due to adsorption on surface of the vessel [17]. Formaldehyde in hydrogen is another example of a mixture that tends not to be stable, also possibly due to loss of compounds to the cylinder walls or degradation reaction between formaldehyde and hydrogen leading to the appearance of by-products [18].

Solutions need to be developed that will allow NMIs and gas standard manufacturers to provide stable mixtures in hydrogen. This can be achieved by identifying suitable passivation treatments which avoid adsorption of reactive species to the cylinder walls [19]. Traceable dynamic standards are an alternative option to static mixtures as they perform in-situ blending of two stable mixtures to temporarily provide an accurate low concentration gas mixture. Further development of gas standards using these methods are required to allow analysis of low level compounds (including ammonia, formaldehyde, formic acid, total sulphur and halogenated compounds) which require traceable and accurate standards.

Measuring 'total' compounds

As shown in Table 1 there are three measurands that specify a 'total' measurement, which includes hydrocarbons, sulphur and halogenated compounds. The difficulty of determining 'total' amount fraction of chemical element (sulphur) or a family of compounds (hydrocarbons or halogenated) is linked to both technical difficulty and to the understanding of 'total'.

The definition of 'total' can easily be misinterpreted. For example, in the case of total hydrocarbons this could either be defined as the summation of all hydrocarbons compounds or as the sum of the total volatile hydrocarbons in the gas sample at a specific temperature. Lack of reference to a standard method may lead to two different results that are both valid. An International Standard that refers to 'total' measurement must therefore be defined within the scope, and only after clear clarification of the definition can analytical methods be reviewed.

The technical difficulty to perform total measurements may also be linked to:

Converting all molecules into individual elements in order to detect the total amount of specific elements (e.g. S, Cl, F, I, Br). Even if the analysis of total amount fraction of a particular element uses classical analytical methodology in inorganic chemistry, it relies on the capability to atomise all molecules in the sample to the basic element. Several issues may arise due to the compound being insoluble or from the inability to atomise some molecules.

Obtaining one signal from various molecules. The measurement of total hydrocarbons can be challenging as it requires the instrument to merge several compounds into one signal. The first challenge is ensuring that all compounds of the family are gathered into the signal. The second challenge is to ensure that interference from other compounds will not lead to false positive or negative results.

Measuring independently all the compounds of a family (hydrocarbons). In theory, it should be possible to provide a 'total' measurement by, for example, analysing all hydrocarbons separately and totalling. However this would require the operator to manually sum the results of limit of detection together (total hydrocarbons could include over 100 different compounds). Summing several compounds may lead to an overestimation of the 'total' result or the operator missing an important compound that was not included during method development.

The benefit of using an analyser that can inherently perform 'total' measurement is that it may be possible to obtain a significantly lower limit of detection compared to summing individual compounds. As an example, for total halogenated measurement the limit of detection for individual halogenated compounds may be 1 nmol mol^{-1} which is significantly lower than required in ISO 14687-2. However, if one considers that there potentially could be more than 50 different halogenated compounds to measure, the limit of detection for total halogenated compounds would be above the specified limit in ISO 14687-2. The paper by Brown et al. further investigates the problem with identifying a suitable method for total halogenated compound measurement [20].

The requirement implied in the use of 'total' for sulphur, hydrocarbons and halogenated in International Standards must be further investigated and following this methods must be identified for performing the measurements. There are standard test methods available for some of these measurements (ASTM standards, such as in ASTM WK23815 [21] and ASTM WK34574 [22]) but these need to be validated to ensure they provide a true 'total' measurement before laboratories

can use them. If the 'total' measurement cannot be performed by any validated method, a recommendation for the key impurities must be provided as an alternative approach. The key impurities would be selected based on a risk assessment of the potential impurities that may be present in the hydrogen following the approach of ISO/DIS 19880-8 [23].

Lack of traceability for particulate measurements

In addition to the gas impurities listed in Table 1 there is also a specification for particulate measurement; the limit for particle mass concentration in fuel cell hydrogen is set at 1 mg m^{-3} as specified in ISO 14687-2. A common approach to performing this measurement in the field is by sampling through a filter for a specified time and measuring the net mass added (the weighing would usually be performed in the laboratory). However, there could be some issues with this approach that have not been studied extensively such as how much of the change in mass could be attributed to particles from the environment (on the blank sample). Additionally, there are some available test methods for particulate mass measurement (such as ASTM D7651-10 [24]) which need to be reviewed and evaluated by an NMI to ensure the method is traceable.

Further work is required to select suitable particle filters for this analysis and to develop a validated method for measuring particulate mass concentration (using a similar approach to ASTM D7651-10). Furthermore, a better understanding of the applied uncertainties is required to ensure the measurement is fit-for-purpose. As an example, an uncertainty may need to be applied to take into account contamination of the particulate filter during transportation. These methods will need to be validated to ensure the specification in ISO 14687-2 can be met.

Laboratory comparability

There are several laboratories worldwide that provide a hydrogen purity testing service, some of which may also have obtained ISO 17025 accreditation for the service through a certified accreditation body. Confidence in analytical results is ensured by various tools: certified reference materials, calibrants, quality control materials, method validation, standard methods and laboratory intercomparison. However, as different tools are used within laboratories (which could create bias) it is important to ensure that the different laboratories provide comparable measurements when analysing the same sample. This will provide confidence in the analytical results and is an important pre-requisite to support decision-makers and end users. International laboratory comparisons are important for demonstrating the equivalence of analytical laboratories. A comparison is a diagnostic tool for detecting systematic or technique bias in participants' results. Benchmarking the hydrogen purity laboratory is crucial in this emerging market as the number of analytical methods and expert knowledge is low with regards to experience with analysing real samples. A pilot study comparison (Euramet 1220 [25]) has already been performed under the EURAMET program for carbon monoxide and hydrogen sulphide in hydrogen (Fig. 1).

During the Euramet 1220 study, participants were asked to provide an amount fraction measurement with uncertainty when analysing a gas mixture containing nominally 1 μmol mol^{-1} of carbon monoxide in hydrogen. This same mixture was circulated around all of the laboratories and each laboratory was allowed two months to provide a measurement using one of their selected analytical techniques. The results have been anonymised except for NPL and Van Swinden Laboratory (VSL) who provided reference values for the study.

A laboratory that has assigned the correct result should provide an uncertainty that overlaps the reference value (normalised to zero in Fig. 1). But a laboratory that does not provide a measurement that overlaps the reference value must consider any bias that has not been accounted for during statistical evaluation and revise the method validation especially (i.e. low uncertainty estimation).

Comparison exercises are crucial for demonstrating that analytical laboratories are able to perform unbiased measurement and report results agreeing with state-of-the-art laboratories. They also allow laboratories to provide evidence for obtaining ISO 17025 accreditation. It provides evidence to demonstrate to external partners or hydrogen users that the results of analysis are accurate and can be trusted to make important decisions (such as whether the hydrogen is compliant with quality requirements set by national regulations). This is particularly important for hydrogen purity testing against ISO 14687-2 as this involves very challenging measurements, in some cases involving novel methods and gas standards.

Quality control

Requirements

Quality control refers to the methods that hydrogen refuelling station operators can use to maintain quality of the hydrogen provided to vehicles as detailed in ISO/DIS 19880-8 [23]. The two methods are spot sampling and monitoring. Spot sampling refers to the process of obtaining a sample of hydrogen gas which is delivered to a laboratory for external purity analysis. The main disadvantage of this method is the long turnaround time; by the time the results are provided to the station many hundreds of cars could have already received contaminated hydrogen. Spot sampling would be a good technique to use during the commissioning stage of the station and as a full quality check on a routine but non-frequent basis to check for the full list of impurities specified in ISO 14687-2.

Online monitoring involves installation of gas and particle analysers capable of performing continuous analysis of the key impurities. Ideally the instrument would be capable of simultaneously monitoring multiple impurities to reduce cost and space taken up by the instrument. Current commercially available instruments however are not able to monitor all impurities listed in ISO 14687-2 and a combination of instruments is required when all analytes need to be detected. Online monitoring is an essential step for preventing harmful impurities from reaching the hydrogen vehicle. The analyser ideally would provide a warning to the operator (or automatically shut down the pump) if the level of the compound being

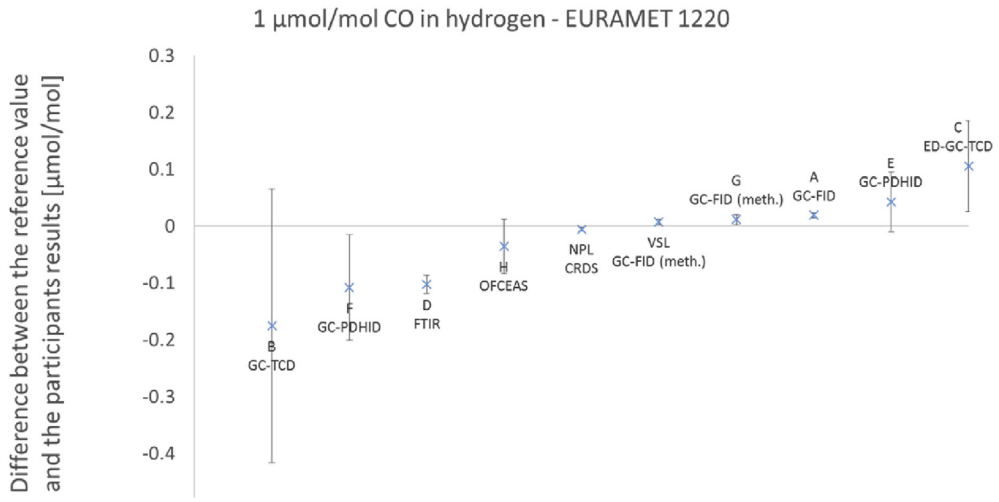

Fig. 1 – EURAMET 1220 international laboratory comparison results for analysis of a 1 µmol mol^{-1} carbon monoxide in hydrogen mixture.

monitored exceeds the maximum amount fraction as specified in ISO 14687-2.

Challenges

Validation of online instruments for gas analysis

There are several instrument manufacturers that provide solutions for online hydrogen purity analysis which are predominantly based on spectroscopy techniques, including Fourier transform infrared (FTIR) spectroscopy, cavity ring down spectroscopy (CRDS), and optical feedback cavity-enhanced absorption spectroscopy (OFCEAS). These instruments are suitable for the detection of most species except for nitrogen, helium, oxygen (except for CRDS) and argon while the specification for sulphur in ISO 14687-2 is close or below the limit of detection of current spectroscopy-based instruments.

Commercially available gas analysers need to be improved to lower the limit of detection and increase accuracy. FTIR spectroscopy enables the simultaneous and rapid detection of multiple critical contaminants at ppb level, including carbon monoxide, carbon dioxide, ammonia, formaldehyde, water and hydrocarbons [26]. However, further method development using this technique is required in order to measure the lower amount fraction thresholds specified in ISO 14687-2. In addition, the performance of four different CRDS-based systems that can accurately detect several critical hydrogen impurities, i.e. water, methane, carbon monoxide, carbon dioxide, ammonia, formaldehyde and oxygen, will be verified and validated [27].

Another incisive analytical tool for the online monitoring of hydrogen contaminants is OFCEAS [28]. A commercially available instrument (AP2E, France) based on this technique should be capable of continuously measuring several critical impurities, including water, carbon monoxide, oxygen and hydrogen sulphide, at the threshold levels specified in ISO 14687. However, evidence of the instrument performance is required through validation against traceable standards and an assessment should be made to obtain important information on performance such as repeatability, linearity, limit of detection and cross-interference between other impurities. Without such testing, it will not be possible to ensure that these instruments are truly capable of providing the required accurate measurements.

Accuracy of commercially available hygrometers

Hygrometers are installed in hydrogen refuelling stations to continuously monitor water levels within the system; in particular this is an important feature of electrolysis-based refuelling stations where water is a possible by-product. There are various types of hygrometers that are commercially available such as metal oxide or chilled mirror dew point. When purchasing such a device from the manufacturer, it is probable that it has not been tested or calibrated under the same conditions as in a refuelling station (for example, it may only have been calibrated with nitrogen or air). From a metrological standpoint the device should be calibrated under the same conditions as the installation point to avoid bias. In addition to testing the accuracy of these devices, it would also be important to assess other factors such as in-service drift and dependency on pressure as once the device is installed in the station it may not be checked for over a year.

Validation of commercially available hygrometers using different sensing principles including metal oxide sensor hygrometers needs to be performed to ensure they are suitable for monitoring water at hydrogen refuelling stations. Further tests including assessment of drift, specificity to hydrogen (compared to a conventional testing gas such as nitrogen) and pressure dependence would also be beneficial in ensuring that these devices are fit-for-purpose.

Online particle analysis

In Section Lack of traceability for particulate measurements offline particle analysis is discussed with a focus on the gravimetric method of weighing a filter. The measurement of particles could be performed directly at the station using an online particle analyser such as a Tapered Element Oscillating Microbalance (TEOM). However, as no studies of this kind

have been performed it is not currently known whether it would be feasible to use such instruments to perform this measurement.

Low cost sensors for hydrogen purity
The use of low cost sensors may be a good strategy for online monitoring of hydrogen purity as specified in ISO 19880-8. The possible limitation of most sensors may be their cross-sensitivity to other analytes. If suitable sensors are available, they will need to be tested using gas mixtures of different compositions (in hydrogen matrix) to check range, accuracy and selectivity.

Sampling

Requirements

Laboratories performing hydrogen purity analysis provide results based on the sample as provided. However, if the sampling performed at the station was not carried our properly or the sample changed composition, this could lead to false results as the received sample would not be representative. There are two scenarios that this could lead to, both with negative outcomes:

- False positive – in this case an impurity would be found in the sample that is not in the hydrogen; this could arise from incorrect sampling leading to ingress of ambient moisture or air. The outcome would be the station fails to meet quality requirements.
- False negative – in this case an impurity that is in the hydrogen provided by the station disappears by the time the sample reaches the laboratory; an example would be low level hydrogen sulphide which could adsorb to stainless steel gas sampling vessels. The outcome would be the hydrogen station appearing to meet quality requirements but in reality providing contaminated hydrogen to customers.

Some guidance on hydrogen sampling at the station is provided in ISO 19880-1 [29] with examples of commercially available sampling equipment for gas and particles but this information does not include how to ensure representative sampling. To avoid false negatives the operator will need detailed information regarding the selection process for sampling vessels or containers. For example, low level hydrogen sulphide or other sulphur compounds may adsorb to stainless steel therefore a recommendation would be to use materials that are passivated with inert coatings such as Silconert® 2000 [30].

Challenges

Procedures for gas sampling at the refuelling station
As mentioned in Section Requirements, to avoid false positives during purity analysis the sampling procedure must ensure that moisture from the sampling lines do not enter the sampling vessel. Additionally, if there are any air leaks within the sampling system this could lead to increased levels of nitrogen or oxygen in the vessel. Representative sampling can be achieved through careful design of the sampling system and effective purging. Although ISO 19880-1 provides some information about sampling, it is too brief to ensure good practice across the hydrogen community. Therefore, robust testing of sampling procedures and vessels must be carried out in order to develop good practice guides.

Representative sampling of particles in hydrogen at the refuelling station
As detailed in ISO 19880-1 the particle mass concentration in the hydrogen can be determined by collecting particles on a suitable filter and measuring the total mass of particles that is trapped per cubic metre of hydrogen. As filters cannot be subjected to high differential pressures the sampling device will need to be able to either provide a low pressure to the filter or ensure that the pressure subjected to the filter is equal on both sides before providing flow. Use of a pressure regulator to reduce the pressure of hydrogen supplied from 700 bar to ambient pressure may lead to loss of particles. A pressure regulator would normally be used to lower the pressure for operation of online particle analysers. If a pressure regulator is to be used before sampling and directly analyse particle mass concentration, a study must be performed to understand how the regulator may contribute to particle loss.

Selection of suitable sampling media
Analytical laboratories may send their own commercial sampling vessels to the station as part of their measurement service. However, ISO 19880-1 does not specify which type of cylinders and materials that should be used. It is only mentioned that the sampling cylinder can typically be a 10 L aluminium canister with a DIN477/1 cylinder connector. As mentioned in Section Requirements some impurities have a propensity to stick to the vessel or react with other components in the gas. Reactions between components and surfaces can largely be avoided by using passivated or treated materials. Therefore, for enabling quality assurance, it is necessary to select the most appropriate vessels for sampling. A study needs to be performed to understand which types of vessels would be suitable for sampling and the potential loss in accuracy that may arise from using the wrong types of vessels.

Conclusions

There are several measurement challenges that need to be addressed to ensure rapid growth of a hydrogen economy. The four challenges (flow metering, quality assurance, quality control and sampling) specified in this paper are associated with International Standards (ISO and OIML). Some of these documentary standards are or will be regulated under national or international (European) directives. National Metrology Institutes are the ideal organisations for developing the metrological infrastructure that underpins these measurements. They are responsible for providing the Primary Standards that link industrial measurements with the SI units. To ensure these measurements are performed comparably across Europe these NMIs will need to collaborate closely to ensure that their own determinations of

Primary Standards are comparable to each other; any disagreement would suggest that there are issues with measurement traceability.

Once the metrology infrastructure is developed, work will be required to disseminate traceability to the hydrogen community through a wide range of activities including open comparison schemes (to assess performance of hydrogen purity laboratories), good practice (guides and workshops) and provision of measurement services such as in-situ flow meter calibrations and hydrogen purity testing in accordance with ISO 14687-2.

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