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Metrology for sustainable hydrogen energy applications. Hydrogen quality specification for fuel cell vehicles

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Abstract. Hydrogen, as an energy source, is a clean and storable solution that could meet the worldwide energy demands in the future. The rapid progress of the fuel cell electric vehicles and related technology will require revising the standards that are too generic to enable a sustainable implementation in this emerging sector. The Reference Gas Laboratory of the National Measurement Institute of Spain (CEM), with academic support from University of Valladolid (UVa), through the 2015 Call for The European Metrology Programme for Innovation and Research (EMPIR), participates in the project "15NRM03 - Hydrogen - Metrology for sustainable hydrogen energy applications" that is coordinated by the Laboratoire National de Métrologie et d'Essais (LNE). This project aims at evaluating the probability of hydrogen impurity affecting fuel cells and developing analytical techniques for traceable measurements of the hydrogen impurity. The project will contribute to the standardisation development works through presentations and informative or normative guides. The Reference Gas Laboratory of the National Measurement Institute of Spain (CEM) is developing optimised methods and gas standards for the hydrogen impurity analysis leading to the implementation of the ISO 14687-2 [1]. In this work, the results of the analysis of impurities of argon, nitrogen, oxygen and helium in first samples will be showed.

1 Introduction

The new European policy objectives in the transport and energy sectors defined in the Horizon 2020 Research and Innovation programme from the European Parliament [2], encourage the decarbonisation of the transport sector by the wide use of hydrogen and strongly promote normative research in order to respond to the specific needs identified in the new European Directive on the deployment of alternative fuels infrastructure 2014/94/EU [3]. Article 5 of the Directive 2014/94/EU establishes the framework of hydrogen supply for road transport by requiring that "the hydrogen refuelling points accessible to the public (…) comply with the specifications set out in point 2 of Annex II". The 2nd point of this referenced Annex II relates to the hydrogen purity dispensed by hydrogen refuelling points that is expected to comply with the technical specifications included in the ISO 14687-2 standard (section 2.2). The metrological needs are identified in ISO 14687-2 as "Since the Fuel Cell Vehicle (FCV) and related technology are developing rapidly, this part of ISO 14687 needs to be revised according to technological progress as necessary probably towards less constraining detection limits". This ISO 14687-2 standard lists the maximum impurity concentrations for particulates and 13 gaseous compounds (Ammonia, Ar, CO, CO_2, formaldehyde, formic acid, H_2O, He, N_2, O_2, total halogenated compounds (HCl), total hydrocarbons compounds, total sulphur compounds) that should not be exceeded in hydrogen supplying a Fuel Cell Electric Vehicle (FCEV). The current recommended methods are not suitable for all the 13 gaseous components mostly due to the very low detection limits which are too close to the specifications listed in the standard. Monitoring these parameters at these low levels of concentrations is both time consuming and expensive as it requires several sampling and analytical techniques to be set up. The performance of analytical methods, existing and under development, will be evaluated to perform hydrogen purity testing (number of parameters covered, uncertainties, risk for interferences, robustness…) with a high level of confidence. New methods will be developed when needed. By defining relevant performance characteristics for methods (selectivity, measurement uncertainties, quantification limits, working range, robustness, trueness and precision…), laboratories would be able to choose adequate analytical methods in terms of the parameter to be studied.

The Reference Gas Laboratory of National Measurement Institute of Spain (CEM) analyses the impurities of argon (Ar), helium (He), nitrogen (N_2) and oxygen (O_2) in real samples of hydrogen. The samples are supplied by hydrogen production plants that use steam methane reforming (SMR), electrolysis or chlor-alkali processes to obtain hydrogen. The analysis of hydrogen samples from a representative number of hydrogen production plants will corroborate the current

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expertise and validate the production process risk assessment with analytical data. The 13 gaseous parameters of ISO 14687-2 (except particulates) will be measured in the hydrogen samples using state-of-the-art methods to reach the values specified in the mentioned standard with the highest precision. If the measured values are lower than the value specified, the analytical methods with the lowest limit of detection will be applied to measure the impurity concentration in the hydrogen samples.

2. Analysis technique

2.1 Preparation of gas standards

To perform the hydrogen purity analysis several calibration standards were prepared. These standards make the measurement traceable to national standards being considered primary reference gas mixtures (PRGMs). The preparation is according to ISO 6142 [4] using gravimetric method and the concentration of these standards was studied to be in a same range of the threshold shown in ISO 14687-2. Argon and nitrogen are added together in the same cylinder using helium as balance gas in order to save time in preparation. The balance gas used for oxygen and helium standards was nitrogen.

Table 1. Concentration of the PRGMs prepared.

Individual contaminant analysed by CEM	Maximum concentration ISO 14687-2 µmol/mol	Concentration of the PRGMs µmol/mol
Argon	100	80, 100, 150
Nitrogen	100	80, 100, 150
Oxygen	5	10, 15, 80
Helium	300	50, 80, 100

2.2 Sample analysis

The first three samples from SMR production process were received in 2 valves cylinder of 0.5 L and labelled as QE1005, QE1018 and QE1024. The cylinders were kept in the laboratory for stabilization during 24 hours before analysis. They are connected to the analyser by a pressure regulator and using stainless steel tubing. The analyser is a micro-GC with Thermal Conductivity Detector (TCD) using a 10 m Molsieve column with a 3 m PLOT-U as a pre-column. The carrier gas used is helium BIP® except when helium is the impurity to be analysed using argon BIP® as carrier gas in that case. The analysis is performed one by one in order of concentration starting with the sampling cylinders and then, the standards. The line is purged 30 s before every analysis.

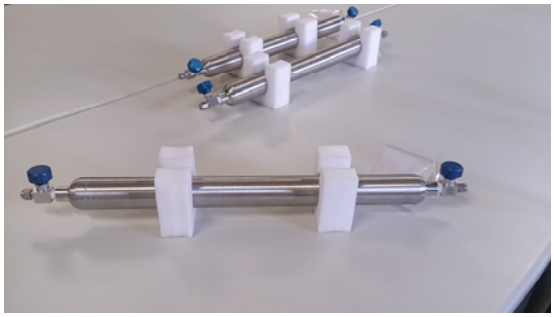

Fig. 1. Sampling cylinders at the laboratory.

3. Impurities analysis

3.1 Oxygen

Two of the samples are analysed and compared to the oxygen in nitrogen PRGMs. The efficiency of the line purging is critical because of the possible presence of oxygen from the ambient air. The number of injections has to be high to minimize the possible effect of the ambient air in the system. This situation can be seen when the chromatographic signal obtained and the number of injection is represented graphically, Fig. 2.

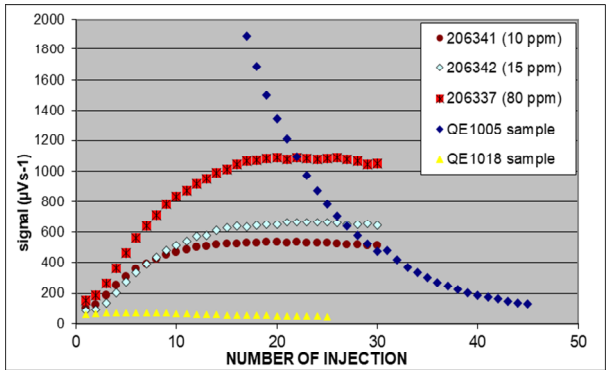

Fig. 2. Graphic presentation for chromatographic signal vs. number of injection for samples (QE1005, QE1018) and PRGMs (10, 15, 80) µmol/mol O_2 in nitrogen.

The graphic presentation of the data is in accordance to the chromatograms obtained. When the chromatograms of PRGMs (5 µmol/mol and 10 µmol/mol O_2 in nitrogen) are compared to samples, it can be seen that the response in the samples is lower than PRGMs response, Fig. 3. Although there is not consistency between the chromatographic signal for standards 5 µmol/mol and 10 µmol/mol, it could be assumed that the amount of oxygen in samples is below 5 µmol/mol, Fig. 2 and Fig. 3.

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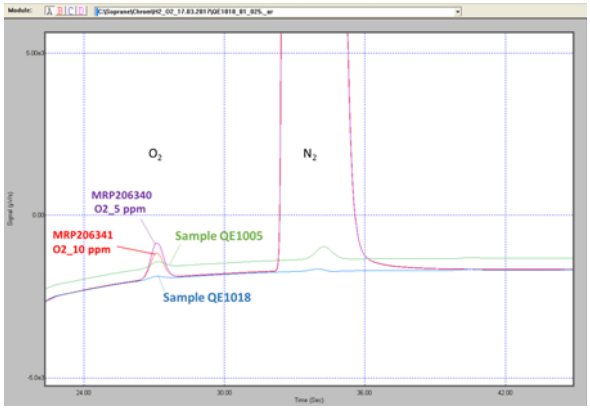

Fig. 3. Comparison of chromatograms for samples (QE1005 and QE1018) and 5 µmol/mol and 10 µmol/mol O_2 in nitrogen PRGMs.

3.2 Helium

The analysis of helium impurities is performed using argon BIP® as carrier gas. The sample QE1018 is analysed and compared with the PRGMs of He in nitrogen. The chromatographic separation of helium and hydrogen peaks in the sample is fundamental. This can be achieved reducing the temperature and the carrier gas pressure increasing the time both analytes are inside the column to force the separation, Fig. 4.

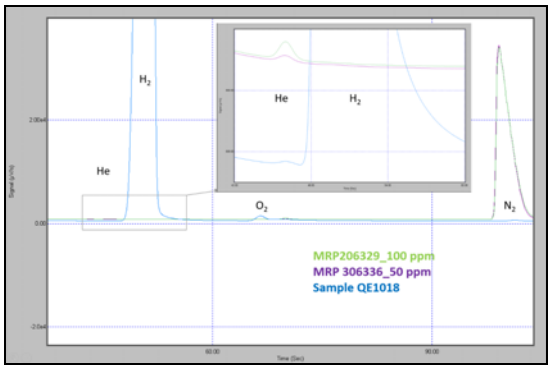

Fig. 4. Chromatograms comparison for sample (QE1018) and PRGMs (50 and 100) µmol/mol He in nitrogen.

If the signal and the number of injection are graphically represented it can be seen that the value of the sample is lower than the 50 µmol/mol PRGM, Fig. 5.

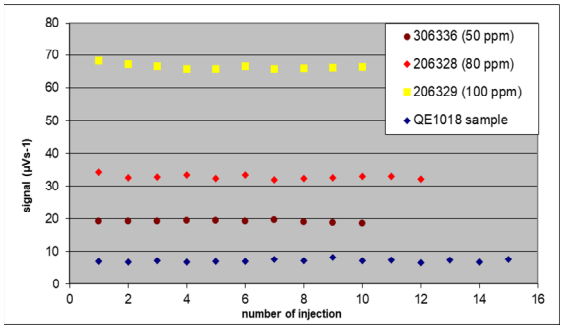

Fig. 5. Graphic presentation for chromatographic signal vs. number of injection for sample (QE1018) and PRGMs (50, 80, and 100) µmol/mol He in nitrogen.

3.3 Argon

The retention time for argon is similar to oxygen so the presence of ambient air in the system because of a poor purge of the lines, can increase the response for argon impurity in the sample. Again a possible solution could be to perform the analysis using a big number of injections, but despite of this, the drift is still too pronounced, Fig. 6.

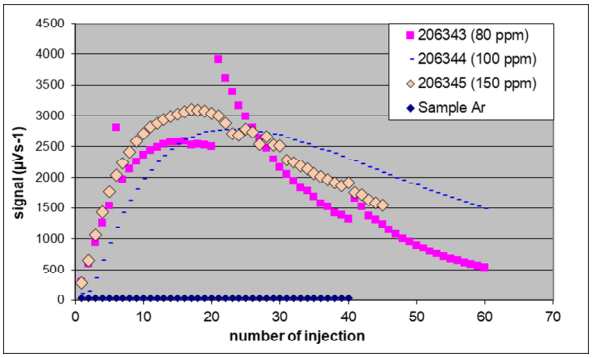

Fig. 6. Graphic presentation for chromatographic signal vs. number of injection for sample (QE1018) and PRGMs (80, 100 and 150) µmol/mol Ar in helium.

The chromatogram obtained for sample (QE1018) and PRGMs is in accordance to the Fig. 6, where it can be seen the value for Ar impurity in the sample is lower than to the PRGMs signals, Fig. 7.

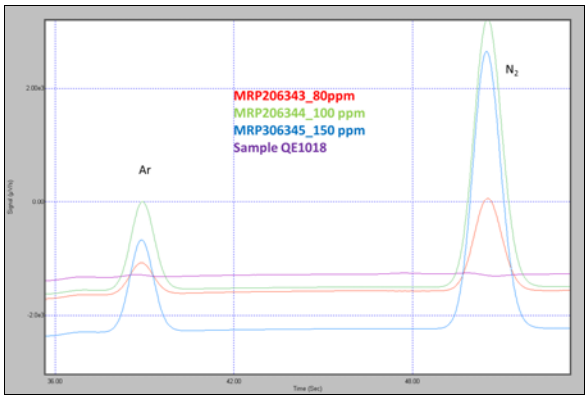

Fig. 7. Chromatograms comparison for sample (QE1018) and (80, 100 and 150) µmol/mol Ar and N_2 in helium PRGMs.

3.4 Nitrogen

With nitrogen the presence of ambient air in lines has the same effect as argon example. If the purge is not effective enough ambient nitrogen can make the signal larger in chromatograms. In this case, it also can be seen a drift in standards signal, Fig. 8. In accordance to chromatogram, the value for sample signal is once again lower than standards value, Fig. 7.

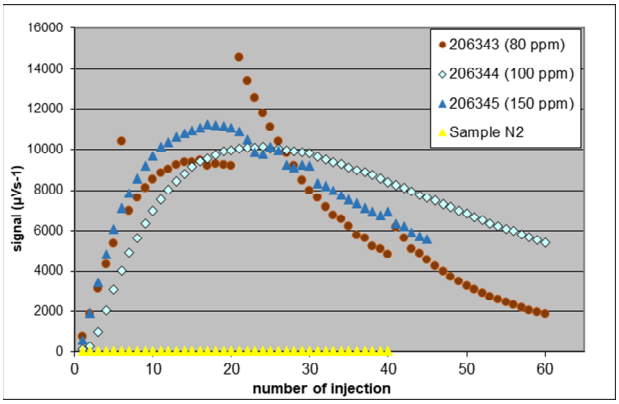

Fig. 8. Graphic presentation for chromatographic signal vs. number of injection for sample (QE1018) and PRGMs (80, 100 and 150) µmol/mol N_2 in helium.

4 Conclusion

The impurity analysis of the samples has been performed using a chromatography separation technique with a thermal conductivity detector. This technique has been shown as efficient in the qualitative determination of the impurities in samples. The gravimetrically prepared gas standards comparison to the samples determinates finally that the level of impurities of oxygen, helium, argon and nitrogen is lower than the threshold value in ISO 14687-2. During the analysis, the purge of the lines would have been fundamental in the achievement of the good results. The presence of ambient air in the system has affected the final results and has made difficult the quantification of the impurities in the samples. The methodology of ISO 6143 [5] using linear calibration with 3 PRGMs is applied to the four compounds. The Goodness-of-fit measure obtained is higher than 2 in all cases so the calibration model is assumed not to be suitable. Further work is required to analyse the next samples and ensure an effective line purging is essential.

This work is linked to the project "15NRM03 - Hydrogen - Metrology for Sustainable Hydrogen Energy Applications" of the European Metrology Programme for Innovation and Research (EMPIR), funded by EURAMET and European Union.

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