

HYDROGEN PURITY ANALYSIS BY FTIR

PROBLEM

Historically, hydrogen has been employed in a variety of industrial chemical processes. Typically, the purity requirements for this hydrogen have tolerated contaminant levels ranging from ppm to low percentages, depending upon the application. The use of hydrogen has now expanded into novel applications such as alternative fuel for use in transportation and stationary electrical generation. These applications demand hydrogen purity levels which place severe demands on the analytical instrumentation employed for gas quality assurance. Thus the development of analytical tools and methods that can simultaneously and accurately detect low levels of multiple contaminants is of critical importance to the implementation of the new energy technologies for transportation and energy generation.

BACKGROUND

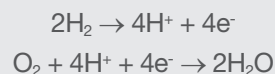
Hydrogen is produced in the petrochemical and chemical industry using hydrocarbon reforming technology. The two main sources for industrial hydrogen are steam reforming of methane (SMR) or other hydrocarbons, and the purified byproduct hydrogen from naphtha reformers, chlorine gas production and other chemical processes. The direct production of hydrogen by electrolysis, a source of hydrogen not based on hydrocarbons, is of obvious interest, however it accounts for less than 0.25% of world hydrogen supplies.

Traditionally, hydrogen has been viewed as an important chemical reactant, particularly for the hydrocarbon cracking processes used in the petrochemical industries. More recently, as the price volatility of fossil fuel has increased

and as concerns over anthropogenic greenhouse gases have heightened, the use of hydrogen as an alternate energy source to fossil fuels has gained tremendous interest, especially for applications such as transportation and electricity generation.

Hydrogen can be converted to energy in two very different ways. Its chemical potential energy can be directly converted to mechanical energy through combustion in an internal combustion engine (ICE), either as a mixture with hydrocarbon fuels or as the pure element. Mixtures of up to 20% hydrogen in natural gas, known as Hythane, can be used in engines adapted for burning natural gas without any further modifications to the engine. The presence of hydrogen in the hydrocarbon allows a much leaner combustion than normal, resulting in improved engine efficiency and greatly reduced emissions, especially NO_x. Mixtures containing more than 30% hydrogen can also be used as fuel in ICEs, but the engines must be specially adapted.

Alternatively, the chemical energy in hydrogen may be converted to electrical energy through an electrochemical reaction in a PEM (Polymer Electrolyte Membrane) fuel cell (Figure 1). The fuel cell reaction is essentially the reverse of electrolysis, generating electricity through the reaction between hydrogen and oxygen to produce water and useable electricity:



Platinum (Pt) catalyst particles on a porous carbon anode dissociate hydrogen molecules to protons and electrons. The electrons pass through the external circuit while the protons diffuse through the PEM to the cathode, combining with the electrons and oxygen from air to produce water.

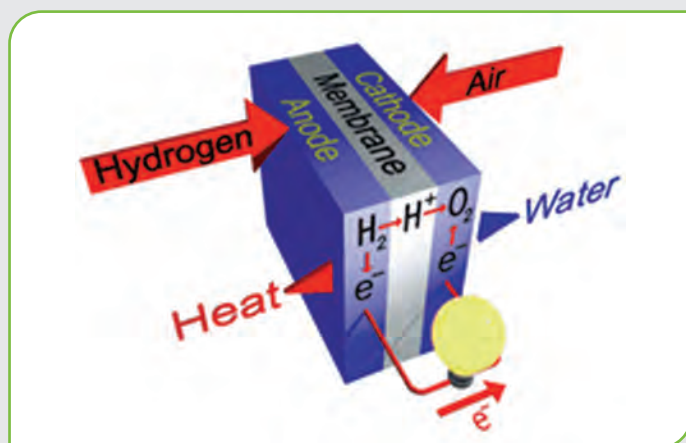
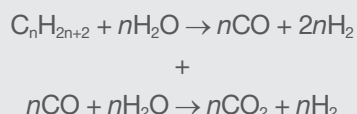


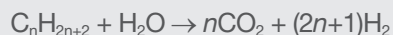
Figure 1 - PEM Fuel Cell

Pt catalysts are extremely sensitive to chemical poisoning and very low contamination levels in the hydrogen feed can poison the catalyst, inducing non-recoverable losses in fuel cell performance (Figure 2). This places extreme demands on the purity of the hydrogen used as fuel to the cell. Maximum allowable levels of certain contaminants are in the ppb range.

Depending upon the source of the hydrogen, the impurities and their concentrations differ. Steam reforming proceeds according to the chemical reaction:



for an overall stoichiometry of:



The chemistry of steam reforming dictates that the primary contaminants in the hydrogen product will derive from the reactants (i.e. C_nH_{2n+2} and H_2O) and byproducts (CO and CO_2). Similarly, the chemistry of other chemical routes to hydrogen results in low levels of H_2S , COS and nitrogen compounds such as NH_3 in the hydrogen product, along with residues of the reactants, hydrocarbon oxidation and other products. Table 1 shows the current SAE 2719 guideline for hydrogen purity in fuel cell applications.

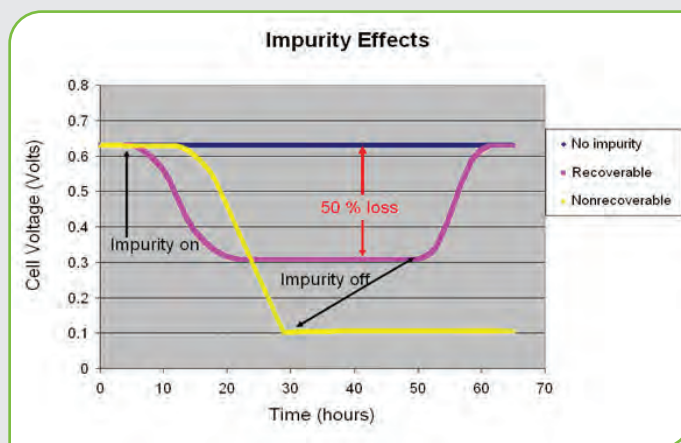


Figure 2 - Hydrogen impurity effects on a PEM fuel cell

The sensitivity of PEM fuel cells to low levels of contamination means that real-time, on-line monitoring of hydrogen quality is critical for efficient operation. Hydrogen quality monitors must be capable of fast and accurate multi-component analyses for species at concentration ranges that can vary from ppb to % level. As well, the analysis must be accurate in the presence of % levels of species such as hydrocarbons and water that can cause serious interferences in some analytical methods. Finally, the analytical data must allow chemical speciation of the contaminants. For cost effectiveness, these characteristics should be present in a single analyzer that can be used for on-line quality monitoring.

Potential Impurity Components	SAE J2719 Maximum Allowable Limits (ppmv)
Ammonia	0.10
Carbon Monoxide (CO)	0.20
Carbon Dioxide	2.00
Formaldehyde (H_2CO)	0.01
Formic Acid ($HCOOH$)	0.20
Total Hydrocarbon (Reported as C_1)	2.00
Methane (CH_4)	0.10
Ethane (C_2H_6)	0.10
Ethylene (C_2H_4)	0.10
Propane (C_3H_8)	0.01
Water (H_2O)	5.00

Table 1 - SAE 2719 Hydrogen Quality Guideline for Fuel Cell Vehicles

SOLUTION

CO, CO₂, NH₃, formaldehyde, H₂O and hydrocarbons, i.e. methane, ethane, etc., are the contaminants of most importance for PEM fuel monitoring. As noted, analytical methods for the detection of these contaminants must be capable of simultaneous and rapid detection of ppb levels in the presence of hydrogen. FTIR is an excellent tool for this analysis in that it can detect all of the contaminant species of interest rapidly and simultaneously; it has detection limits in the ppb regime; and it can tolerate analyte interferences.

The MKS MultiGas™ Analyzer, Model 2031 is a low maintenance, low cost FTIR analyzer that is an effective solution for simultaneous multi-component analyses of contaminants in hydrogen. It can be integrated as an on-line hydrogen quality monitor in a variety of configurations, including at the outlet of a reforming plant, as a monitor prior to gas cylinder filling, and as a qualifier for hydrogen from gas cylinders as well as on site at a fuel filling station.

FTIR Method Validation

Our FTIR Method Validation was performed in accordance with ASTM D7653-10 Standard Test Method for Determination of Trace Gaseous Contaminants in Hydrogen Fuel by Fourier Transform Infrared (FTIR) Spectroscopy.

NIST traceable calibration standards were used in the method validation. These standards were obtained with 100 ppm of the selected contaminants in bulk H₂; lower concentrations were produced using the gas manifold shown in Figure 3. Multiple sample concentrations were created using the gas blending system and analyzed by the MultiGas Analyzer, Model 2031 during the course of the method validation. A hydrogen purifier was installed on the H₂ bulk gas for use with hydrogen blank samples and dilution hydrogen. In order to minimize instrument errors, repeat samples with duplicate concentrations were analyzed with the MFCs swapped between the gas feed lines. At least seven repeat analyses were performed at the maximum and minimum contaminant concentration values.

Method detection limits (MDLs) were determined in accordance with EPA 40 CFR Part 136 Guidelines Establishing Test Procedures for Analysis of Pollutants, Appendix B – Definition and Procedures for the Determination of the Method Detection Limit – Revision 1.11.

Blanks employed in the validation were purified H₂ with no detectable impurities in accordance with the Guideline. The first estimate of the method detection limit was three times the standard deviation of replicate samples as per the Guideline. The second set of data analysis employed seven repeat measurements made at the detection limit.

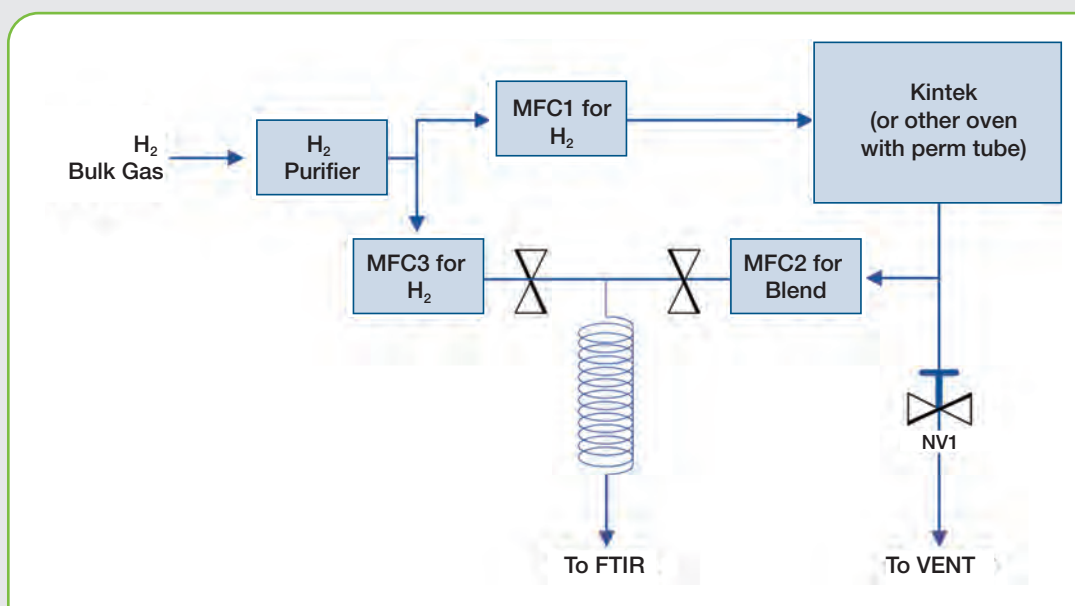


Figure 3 - Gas blending apparatus

The variance was determined on seven measurements at a single concentration. Variances determined on the same concentration were determined only on the median of seven replicates. This verifies that the error is mainly due to the instrument and not to the MFCs. Confidence limits of 99% were applied using the Student t-test.

The tests used two detectors: a 16 μ MCT high sensitivity LN₂-cooled detector and a 9.2 μ MCT lower sensitivity detector with thermoelectric (TE) cooling. The 16 μ detector requires no maintenance other than daily filling with liquid nitrogen (every three days when equipped with an extended 5L dewar). The 9.2 μ TE detector requires no maintenance at all and could be used 24/7 since no liquid nitrogen is needed. It is, however, less sensitive to alkenes and some other species due to detector cutoff. Figure 4 shows the detector cutoffs and the positions of relevant absorption frequencies for the contaminants of interest.

Table 2 shows the results of the method validation along with the regulatory detection limits, as defined in SAE J2719. The data in Table 2 show that the minimum detection levels for CO, CO₂, formaldehyde, formic acid, CH₄, C₂H₆, and water are all within or significantly better than the Guideline when using a MultiGas Analyzer, Model 2031 equipped with the 16u LN₂-cooled detector.

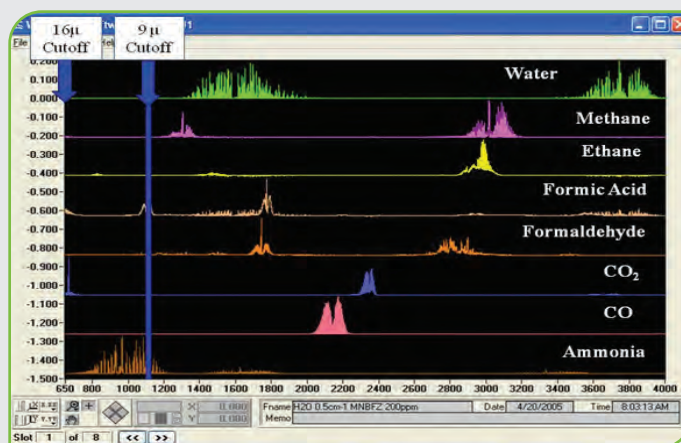


Figure 4 - LN₂ vs. TE detector cutoff relative to contaminant absorbance positions

For ammonia (NH₃) analyses, the MultiGas Analyzer, Model 2031, equipped with the 16 μ LN₂-cooled detector exhibits suitable MDLs; however the 9.2 μ TE cooled detector has a MDL significantly higher than the Guideline.

The method validation results have shown that the MultiGas™ FTIR Gas Analyzer, Model 2031 is well suited for the determination of contaminant levels in hydrogen intended for PEM fuel cell use for almost all of the listed components. The Model 2031 analytical method developed for the analysis of impurities in hydrogen has been proven to have sufficiently low MDLs to effectively guard a fuel cell

Potential Impurity Components	SAE J2719 Maximum Allowable Limits (ppmv)	Model 2031 TE, 9u (1 σ for 7 Samples) (ppmv)	Model 2031 LN ₂ , 16u (1 σ for 7 Samples) (ppmv)
Ammonia	0.10	0.33	0.02
Carbon Monoxide (CO)	0.20	0.02	0.01
Carbon Dioxide	2.00	0.01	0.01
Formaldehyde (H ₂ CO)	0.01	0.01	0.01
Water (H ₂ O)	5.00	0.30	0.05
Formic Acid (HCOOH)	0.20	0.01	0.01
Total Hydrocarbon (Reported as C ₁)	2.00		
Methane (CH ₄)	0.10	0.01	0.01
Ethane (C ₂ H ₆)	0.10	0.02	0.02
Ethylene (C ₂ H ₄)	0.10		0.01
Propane (C ₃ H ₈)	0.10		0.02

Table 2 - SAE J2719 and MultiGas Analyzer, Model 2031 minimum detection limits (MDLs)

gas feed against all of the contaminants having significant negative impact on PEM performance. The Model 2031 is thus an effective gas quality monitor for hydrogen in PEM fuel cell applications.

CONCLUSION

Challenge testing has shown that the MultiGas Analyzer, Model 2031 is a highly repeatable, accurate and precise analytical tool for the simultaneous detection of the contaminants important for quality monitoring of the hydrogen fuel to PEM fuel cells. The Model 2031 can be used on-line for continuous monitoring of multiple contaminants, even in the presence of high concentrations of interfering species such as water. Analytical methods developed based on the MultiGas Analyzer, Model 2031 equipped with appropriate detectors have demonstrated minimum detection limits in full compliance with the SAE J2719 guideline for hydrogen quality in fuel cell applications.