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System

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EXECUTIVE SUMMARY

This report presents the results of work carried out at NPL between February 2010 and March 2011 to develop traceable methods for the measurement of trace-levels impurities in hydrogen for fuel cell applications. Experimental results are presented and discussed, and the limits of detection of each method developed are assessed against those in International Standards. It should be noted that this report summarises NPL's suite of analysis methods as of the date of this report (August 2011); suggestions for further development of the work are also given.

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EXECUTIVE SUMMARY

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1 INTRODUCTION

The use of hydrogen as a power source for stationary appliances and road vehicles is expected to play a significant role in the UK's efforts to reduce the proportion of fossil fuels in its energy portfolio as the Government strives to meet its commitment of reducing the UK's carbon dioxide emissions by 80% by 2050 [1].

At present, industrial hydrogen is mainly manufactured by the steam reformation of hydrocarbons, which involves a high temperature reaction of methane (or other hydrocarbons such as butane) with water to form carbon monoxide and hydrogen; normally in subsequent combination with a lower temperature shift reduction of water by carbon monoxide to form carbon dioxide and additional hydrogen. The hydrogen is then purified using a range of separation technologies such as the use of membranes or pressure swing adsorption.

An alternative, and potentially much 'greener' method to manufacture hydrogen is electrolysis – the carbon footprint of such a method is very low if the electricity is produced using a renewable energy source. One potential problem with renewable technologies (such as photovoltaic solar panels or wind turbines) is their sporadic and sometimes unpredictable production of power, so as the use of renewable technologies becomes more widespread, so does the requirement to store energy that is not used immediately. The electrolysis of water to form hydrogen offers a unique means of energy storage, allowing excess power to be stored as a compressed gas indefinitely, so that it may be used when it is required, for example by reaction in a fuel cell.

A large number of fuel cell devices have been commercialised as power sources for stationary applications, such as back-up power generation, facilitating remote or off-grid energy storage or as heat and power co-generation systems. Currently, many stationary polyelectrolyte membrane (PEM) fuel cells are equipped with a reformer that converts fossil fuel to hydrogen-rich fuel composed primarily of hydrogen and carbon dioxide; other stationary fuel cells use hydrogen of high quality, supplied through high-pressure cylinders or tanks, by pipeline from a distant hydrogen production plant, from on-site vaporisation of liquefied hydrogen or on-site electrolysis.

Another highly promising area for the future use of hydrogen is in road vehicles, powered by either fuel cells or hydrogen burning internal combustion engines – in fact, a small fleet of hydrogen powered vehicles are already on the UK's roads and a number of refuelling stations (mainly at research institutions) are in operation. Hydrogen fuelled internal combustion engine vehicles offer a short- to intermediate-term alternative to conventionally fuelled vehicles, with vastly reduced exhaust emissions, whereas the development of hydrogen fuel cell vehicles offers substantial increases in efficiency and further reductions in exhaust emissions, with the elimination of nitrogen oxides. The development and deployment of new and sustainable fuels and propulsion systems is a goal outlined in the European Commission White Paper '*Roadmap to a Single European Transport Area – Towards a competitive and resource efficient transport system*' [2].

The future uptake of hydrogen as a fuel is highly dependent on the ability to produce low cost hydrogen, which is of a sufficient purity, as the presence of impurities at even trace levels (parts-per-million (ppm) or parts-per-billion (ppb)) can severely affect the performance of fuel cells. These purity requirements, which are applicable to hydrogen generated by any industrial method, are currently being set out in the draft International Standards ISO/DIS 14687-2 [3] and ISO/WD 14687-3 [4], with differing purities depending on the appliance in question. These specifications are presented in Section 2 of this report.

The remainder of this report firstly discusses the challenges of developing traceable methods for the analysis of trace-level impurities in hydrogen (Section 3), before presenting and discussing the methods developed during the course of this work, and comparing the limits of detection of these methods with the specifications in ISO/DIS 14687-2 and ISO/WD 14687-3 (Section 4). Some results from the analysis samples of hydrogen from small-scale electrolyser devices using these analytical methods are then given for illustration in Section 5.

2 DRAFT INTERNATIONAL STANDARDS ISO 14687-2 & 14687-3

As described in the introduction, two International Standards are currently being drafted which specify the purity requirements for hydrogen for fuel cell applications, namely:

- ISO/DIS 14687-2: *Hydrogen fuel — Product specification — Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles*. Development of this Standard is being carried out by ISO TC197/WG12; a Draft International Standard (DIS) version was submitted for voting in January 2011.

- ISO/WD 14687-3: *Hydrogen fuel — Product specification — Part 3: Proton exchange membrane (PEM) fuel cell applications for stationary appliances*. Development of this Standard is being carried out by ISO TC197/WG14; a working draft (WD) version was circulated to working group members in July 2011

The aim of this work presented in this report was to develop traceable methods for key impurity species with analytical limits of detection below the fuel quality requirements specified by these draft ISO Standards (see Table 1). Note that as the draft Standards are still under development, the content of Table 1 is presented as correct as of the date of this report (August 2011).

Component	**Maximum impurity concentration (in µmol/mol unless stated)**			
	Types I & II Grade D	**Type I Grade E Category 1**	**Type I Grade E Category 2**	**Type I Grade E Category 3**
Water	5	See note (a)	See note (a)	See note (a)
Total hydrocarbons cmpds*	2	10	2	2
Oxygen	5	200	200	5
Helium	300	400,000	400,000	1,000
Nitrogen	100	400,000	400,000	1,000
Argon	100	400,000	400,000	1,000
Carbon dioxide	2	See note (b)	See note (b)	2
Carbon monoxide	0.2	10	10	0.2
Total sulphur compounds	0.004	0.004	0.004	0.004
Formaldehyde	0.01	3	0.01	0.01
Formic acid	0.2	12	0.2	0.2
Ammonia	0.1	0.1	0.1	0.1
Total halogenated compounds	0.05	0.05	0.05	0.05
Particulate concentration	1 mg/kg	1 mg/kg	1 mg/kg	1 mg/kg

Table 1. Fuel quality requirements specified by ISO/DIS 14687-2 (Types I & II Grade D) and ISO/WD 14687-3 (Type I Grade E). The grades of hydrogen relate to:

- Type I Grade D: Gaseous hydrogen fuel for PEM fuel cell road vehicle systems.
- Type II Grade D: Liquid hydrogen fuel for PEM fuel cell road vehicle systems.
- Type I Grade E Category 1: Gaseous hydrogen fuel for PEM fuel cell applications for stationary appliance systems (for high efficiency applications: 50 % minimum hydrogen).
- Type I Grade E Category 2: Gaseous hydrogen fuel for PEM fuel cell applications for stationary appliance systems (for high load applications: 50 % minimum hydrogen).
- Type I Grade E Category 3: Gaseous hydrogen fuel for PEM fuel cell applications for stationary appliance systems (for high fuel index hydrogen applications: 99.9 % minimum hydrogen).

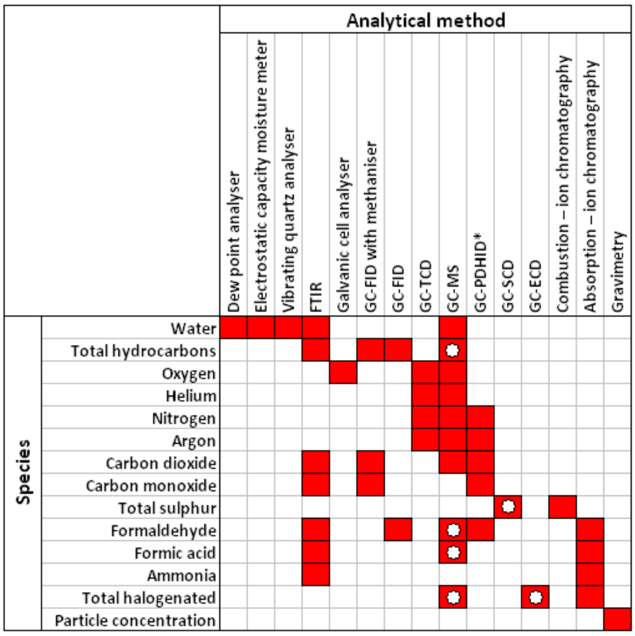
* The specification for total hydrocarbons is stated as a methane basis.
Note (a): specified as non-condensing at ambient conditions.
Note (b): specified as 'included in total non-hydrogen gases' (max 50 % mol/mol).

The data in Table 1 shows that the most stringent purity requirement is for the Types I & II Grade D hydrogen specified by ISO/DIS 14687-2 - the limits of detection of the methods developed in this report are compared against this specification in Section 4.

3 ANALYTICAL CHALLENGES

The hydrogen purity requirements specified by the ISO 14687 family of draft Standards (as shown in Table 1), present a series of analytical challenges, the majority of which arise from the very low amount fractions specified for some components.

The large number of components in the ISO specifications is also problematic from an analytical perspective as it is not possible to analyse all the components using a single analytical method. Figure 1 summarises the possible analytical methods specified by ISO/DIS 14687-2, and this shows that GC-MS is a good candidate method to perform the simultaneous analysis of a large number of components. The fact that multiple analytical techniques are required means that a large sample volume of hydrogen at high pressure may be required – this is especially the case when using one or more analytical methods that require a large volume of sample, such as cavity ring-down spectroscopy or ion chromatography.



		Analytical method														
		Dew point analyser	Electrostatic capacity moisture meter	Vibrating quartz analyser	FTIR	Galvanic cell analyser	GC-FID with methaniser	GC-FID	GC-TCD	GC-MS	GC-PDHID*	GC-SCD	GC-ECD	Combustion – ion chromatography	Absorption – ion chromatography	Gravimetry
Species	Water	🟥	🟥	🟥	🟥					🟥						
	Total hydrocarbons				🟥		🟥	🟥		○						
	Oxygen					🟥			🟥	🟥						
	Helium								🟥	🟥						
	Nitrogen								🟥	🟥	🟥					
	Argon								🟥	🟥	🟥					
	Carbon dioxide				🟥		🟥			🟥	🟥					
	Carbon monoxide				🟥		🟥				🟥					
	Total sulphur											○		🟥		
	Formaldehyde				🟥			🟥		○	🟥				🟥	
	Formic acid				🟥					○					🟥	
	Ammonia				🟥										🟥	
	Total halogenated									○			○		🟥	
	Particle concentration															🟥

○ = with pre-concentration device
*** GC-pulsed discharge helium ionization detector**

Figure 1. Summary of analysis methods specified by ISO/DIS 14687-2.

An additional challenge is that a number of the components in Table 1 are unstable and/or reactive. In order to obtain accurate analytical results, passivated sampling vessels are therefore needed, and extreme care also has to be taken during analysis to ensure that these components at these very low concentrations do not adsorb to sample lines and other analytical equipment such as regulators, connectors and valves.

Furthermore, whilst accurate and traceable calibration gas mixtures in cylinders are available for a number of the components in Table 1 (*e.g.* oxygen, nitrogen and carbon dioxide), this is not true for components such as water and formaldehyde. (NPL is however working towards developing stable gas standards of both water and formaldehyde in cylinders at low-ppm levels; some of these standards have been used in the experimental work discussed in Section 4). This therefore means that if the analysis is required to be traceable to national standards, an alternative calibration method must be used, for example using a permeation device for water.

Finally, the representative sampling of hydrogen is key in ensuring the accurate measurement of hydrogen - it is crucially important that the sample is not contaminated (with for example air or particulates) in order to obtain valid analytical results. Sampling of hydrogen is not discussed in detail in the report, but NPL has developed an in-house method for sampling hydrogen from low-pressure sources, and commercial devices are becoming available for sampling hydrogen from high-pressure sources (*e.g.* hydrogen at 700 bar from vehicle refuelling stations). An ASTM Standard method is also being developed for high-pressure hydrogen sampling [5].

4 ANALYTICAL METHODS

4.1 OVERVIEW

This section first takes each of the components in Table 1 in turn and describes briefly the analytical methods developed during the course of this work. Where relevant, the methods are illustrated by chromatograms from the analyses of gas standards, or the analysis of samples of industrially produced or electrolytic hydrogen, and the calculated limit of detection is compared against the purity specification in ISO/DIS 14687-2. It should be noted that results and data presented in this section summarises NPL's suite of analysis methods as of the date of this report (August 2011).

Some typical results from the use of this method to analyse samples of hydrogen from small-scale electrolyser devices are then given for illustration in Section 5.

4.2 METHODS DEVELOPED

4.2.1 Water

(a) CRDS (cavity ring-down spectroscopy)

Calibration:	Water permeation device with a novel dilution system
Limit of detection:	0.01 µmol/mol
ISO/DIS 14687-2 specification:	5 µmol/mol

The response of the CRDS analyser with time when used to analyse a cylinder of Air Products BIP+ hydrogen is shown in Figure 2. A final, stable reading of 16.5 nmol/mol of water was obtained, which is in agreement with the specification of the cylinder (water < 20 nmol/mol).

It is clear from Figure 2 that a significant period of time was taken to reach this result, but there is potential to reduce the analysis time with improved purging of the system prior to the commencement of analysis. However, CRDS does require a large flow rate of sample (approximately 500 ml.min^{-1} for the instrument used here), and so, despite the very low limit of detection, CRDS is unlikely to be suitable for the analysis of small volume samples of hydrogen.

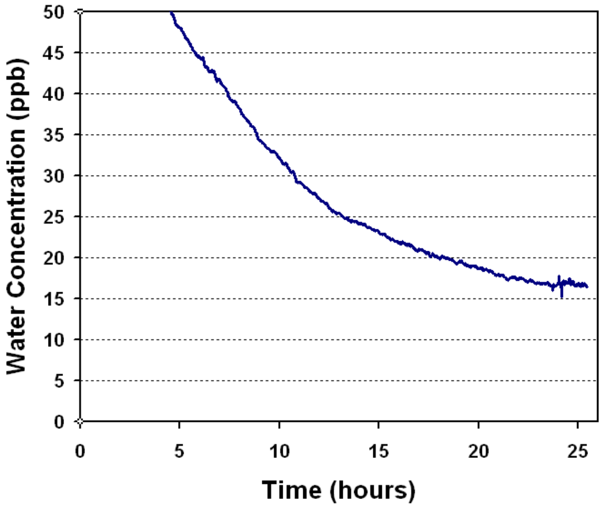


Figure 2. Analysis of the water content of a cylinder of Air Products BIP+ hydrogen using CRDS.

(b) GC-MS (gas chromatography – mass spectroscopy)

Calibration: Calibration gas mixture (approx 20 µmol/mol water in nitrogen)
Limit of detection: 0.8 µmol/mol
ISO/DIS 14687-2 specification: 5 µmol/mol

Figure 3 shows the GC-MS peak obtained from the analysis of the 20 µmol/mol calibration gas mixture using single ion monitoring (*m*/*z* = 18).

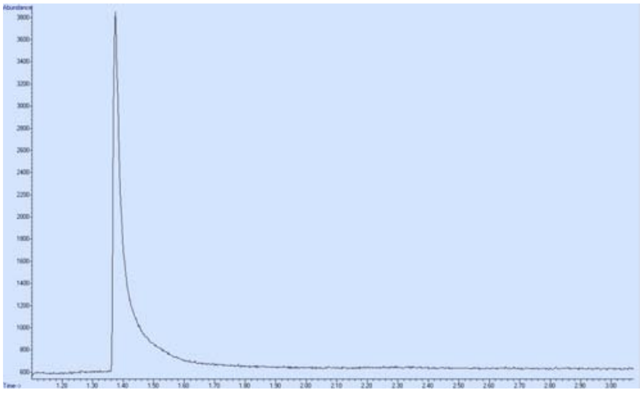


Figure 3. Chromatogram obtained from the GC-MS analysis of a 20 µmol/mol water in nitrogen calibration gas mixture, using single ion monitoring mode (*m*/*z* = 18).

This GC-MS method has great potential for measuring water in hydrogen with a limit of detection below that specified in ISO/DIS 14687-2. A major benefit of GC-MS analysis is that a much smaller sample volume is required than for CRDS, although it is crucial to ensure that all surface of the sample lines, regulators, connectors, *etc.* are fully passivated. This can be assisted by the use of a vacuum to remove any residual water from the system prior to analysis. Care must also be taken to ensure that the GC-MS method avoids co-elution of water with other components that contain the same molecular mass fragment.

It should also be noted that although a lower concentration calibration gas mixture would have ideally been used to calibrate the GC-MS, stable gas mixtures of water vapour are still under development and the preparation of stable mixtures with concentrations of less than approximately 10 µmol/mol is challenging.

(c) Other candidate methods

Other possible methods for the analysis of water in hydrogen include: ceramic sensor hygrometry, a quartz-crystal microbalance, and FTIR spectroscopy.

4.2.2 Total hydrocarbon components

(a) Measurement of total hydrocarbons using a methaniser and GC-FID (gas chromatography – flame ionisation detection)

Calibration:	Calibration gas mixture (see Table 2)
Limit of detection:	0.01 µmol/mol
ISO/DIS 14687-2 specification:	5 µmol/mol

Figure 4 shows an example chromatogram obtained from the analysis of a sample of electrolytic hydrogen using a methaniser - GC-FID system. Calibration of the instrument took place using a traceable gas mixture prepared at NPL (see Table 2).

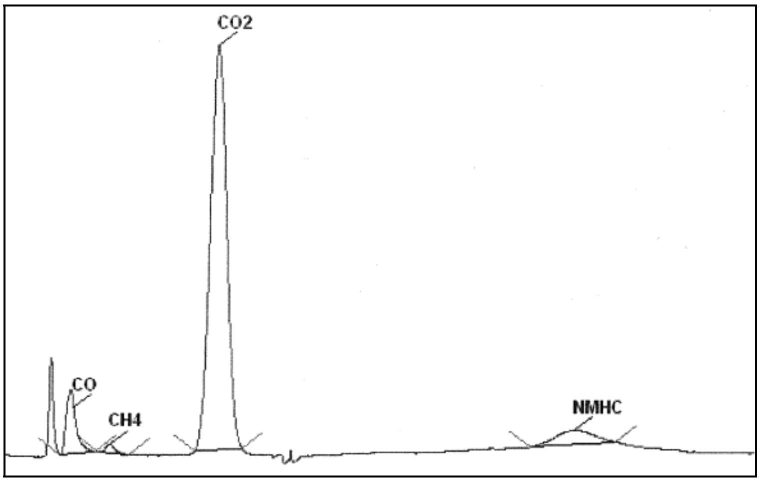


Figure 4. Chromatogram obtained from the methaniser - GC-FID analysis of a sample of electrolytic hydrogen. The labelled peaks are carbon monoxide (CO), methane (CH4), carbon dioxide (CO2) and non-methane hydrocarbons (NMHC).

Component	Amount fraction (µmol/mol)
Methane	13.88
Oxygen	14.89
Helium	268.9
Nitrogen	16.31
Carbon dioxide	13.91
Carbon monoxide	14.88
Hydrogen	balance

Table 2. Calibration gas mixture prepared at NPL for the measurements of total hydrocarbons, methane, oxygen, helium, nitrogen, carbon dioxide and carbon monoxide presented in this report

Figure 4 shows that methane is measured separately to the other (non-methane) hydrocarbon components, which are backflushed from the GC column towards the end of the analytical cycle. The calculated amount fractions of methane and non-methane hydrocarbons are therefore summed to give the amount fraction of total hydrocarbon components.

This methaniser - GC-FID method allows the analysis of hydrocarbons to be carried out rapidly and using only a small volume of hydrogen, whilst still achieving a limit of detection much lower than that specified in ISO/DIS 14687-2. A disadvantage of this method is that the instrument is a process GC designed to operate with minimum user intervention, meaning that there is very limited functionality for the operator to modify settings such as integration parameters.

(b) Measurement of methane using GC-PDHID (gas chromatography – [pulsed] discharge helium ionisation detection)

Calibration: Calibration gas mixture (see Table 2)
Limit of detection: 0.006 µmol/mol
ISO/DIS 14687-2 specification: Not applicable (only specified for total hydrocarbon components)

A method was also developed to measure methane using a GC-PDHID – an example chromatogram is shown in Figure 5. Although the limit of detection for methane is lower than that achievable with the methaniser - GC-FID, the GC-PDHID instrument at NPL does not have the capability to measure total hydrocarbon components by the use of backflushing. A system could however be designed to [erform backflushing if required.

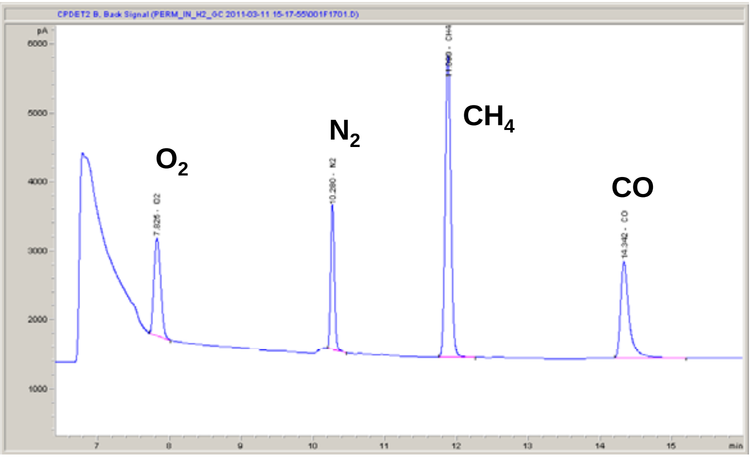


Figure 5. Chromatogram obtained from the GC-PDHID analysis of a calibration gas mixture. The labelled peaks are oxygen (O_2), nitrogen (N_2) methane (CH_4) and carbon monoxide (CO).

(c) Other candidate methods

Other possible methods for the analysis of hydrocarbon components in hydrogen include: GC-FID, FTIR spectroscopy, GC-MS with pre-concentration, and CRDS.

4.2.3 Oxygen

(a) GC-PDHID

Calibration:	Calibration gas mixture (see Table 2)
Limit of detection:	0.006 µmol/mol
ISO/DIS 14687-2 specification:	5 µmol/mol

An example chromatogram from the GC-PDHID method is shown in Figure. 5 The limit of detection obtained for oxygen is far lower that than specified in ISO/DIS 14687-2, and in fact Figure 1 shows that ISO/DIS 14687-2 does not actually state GC-PDHID as a possible method of analysis for oxygen, which is an omission from the draft Standard.

(b) GC-TCD (gas chromatography – thermal conductivity detection)

Calibration:	Calibration gas mixture (see Table 2)
Limit of detection:	3 µmol/mol
ISO/DIS 14687-2 specification:	5 µmol/mol

An alternative method for the analysis of oxygen in hydrogen is GC-TCD. Gas chromatograms equipped with TCDs are far more widely used than GC-PDHIDs, but this method does have a significantly higher limit of detection (although, importantly, it is also less than that specified in ISO/DIS 14687-2).

Figure 6 shows the GC-TCD chromatogram obtained from two samples of electrolytic hydrogen measured repeatedly a number of times. The presence of oxygen is sample 1 (and the absence of oxygen from sample 2) can clearly been seen, as can the good repeatability of these measurements, even at these trace levels.

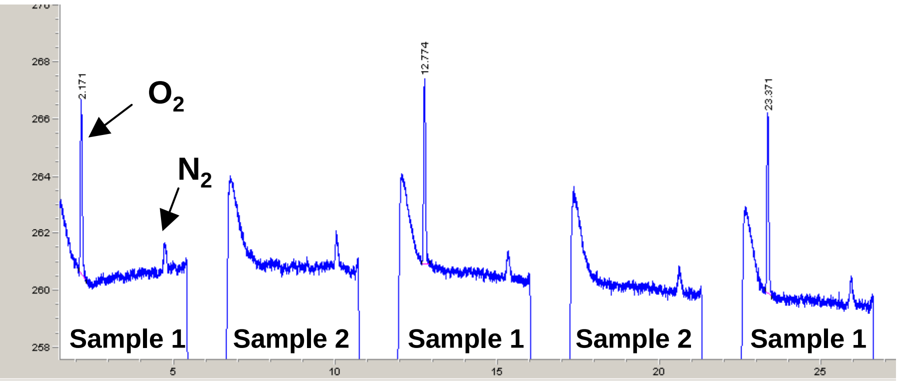


Figure 6. Chromatogram obtained from the GC-TCD analysis of two samples of electrolytic hydrogen. The labelled peaks are oxygen (O_2) and nitrogen (N_2).

(c) Other candidate methods

Other possible methods for the analysis of oxygen in hydrogen include: GC-MS, CRDS, a galvanic cell type oxygen analyzer, and a coulometric sensor.

4.2.4 Helium

(a) GC-TCD

Calibration: Calibration gas mixture (see Table 2)
Limit of detection: 13 µmol/mol
ISO/DIS 14687-2 specification: 300 µmol/mol

Analysis of helium to a limit of detection of less than 300 µmol/mol does not provide an analytical challenge, but care has to be taken in selecting the GC carrier gas - a helium carrier gas can obviously not be used. For this work, the analysis has been performed successfully using both hydrogen and argon carrier gases, although sufficiently pure carrier gas must be used so that a false positive is not recorded when analysing samples of hydrogen. The carrier gas must therefore be validated as fit-for-purpose prior to use.

(b) Other candidate methods

GC-MS is another possible method for the analysis of nitrogen in hydrogen.

4.2.5 Nitrogen

(a) GC-PDHID

Calibration: Calibration gas mixture (see Table 2)
Limit of detection: 0.003 µmol/mol
ISO/DIS 14687-2 specification: 100 µmol/mol

Figure 5 shows an example chromatogram for the analysis of nitrogen by GC-PDHID. As is the case with oxygen, the GC-PDHID method has a limit of detection far lower than that specified in ISO/DIS 14687-2. Indeed, the analysis of nitrogen to a limit of detection of less than 100 µmol/mol does not provide an analytical challenge.

(b) GC-TCD

Calibration: Calibration gas mixture (see Table 2)
Limit of detection: 8 µmol/mol
ISO/DIS 14687-2 specification: 100 µmol/mol

Figure 6 shows an example chromatogram for the analysis of nitrogen by GC-TCD. The calculated limit of detection is much higher than that of the GC-PDHID method, but is still less than that specified in ISO/DIS 14687-2.

(c) Other candidate methods

GC-MS is another possible method for the analysis of nitrogen in hydrogen.

4.2.6 Argon

(a) GC-TCD

Calibration: Calibration gas mixture (approx. 100 µmol/mol argon in nitrogen)
Limit of detection: 5 µmol/mol
ISO/DIS 14687-2 specification: 100 µmol/mol

As for helium, the analysis of argon can be carried out using GC-TCD, provided that a method is used that separates argon from oxygen. For this work, such a method was developed using a 60 m PLOT MS-5 column and helium carrier gas (although hydrogen carrier gas could equally be used), which allowed argon to be measured with a limit of detection of approximately 5 µmol/mol, significantly lower than the specification in ISO/DIS 14687-2.

(b) GC-PDHID

As specified in Figure 1, argon can also be measured using GC-PDHID. Although GC-PDHID was not used for the analysis of argon in hydrogen during this study, a method has subsequently been developed with a limit of detection of 0.01 µmol/mol. This is much lower than the limit of detection of the above GC-TCD method (although this already exceeds the specifications in ISO/DIS 14687-2).

(c) Other candidate methods

GC-MS is another possible method for the analysis of argon in hydrogen.

4.2.7 Carbon dioxide

(a) Methaniser - GC-FID

Calibration: Calibration gas mixture (see Table 2)
Limit of detection: 0.015 µmol/mol
ISO/DIS 14687-2 specification: 2 µmol/mol

Carbon dioxide was successfully measured using the methaniser - GC-FID system – an example chromatogram is shown in Figure 4.

(b) GC-PDHID

Although GC-PDHID was not used for the analysis of carbon dioxide in hydrogen during this study, a method has subsequently been developed with approximately the same limit of detection as the methaniser - GC-TCD method (0.015 µmol/mol). The use of either of these methods therefore results in a limit of detection that far exceeds the specifications in ISO/DIS 14687-2.

(c) Other candidate methods

Other possible methods for the analysis of carbon dioxide in hydrogen include: GC-TCD, GC-MS, and FTIR spectroscopy.

4.2.8 Carbon monoxide

(a) GC-PDHID

Calibration: Calibration gas mixture (see Table 2)
Limit of detection: 0.012 µmol/mol
ISO/DIS 14687-2 specification: 0.2 µmol/mol

Figure 5 shows an example chromatogram for the analysis of carbon monoxide by GC-PDHID.

(b) GC-TCD

Calibration: Calibration gas mixture (see Table 2)
Limit of detection: 0.04 µmol/mol
ISO/DIS 14687-2 specification: 0.2 µmol/mol

Both the GC-PDHID and GC-TCD methods developed measure carbon monoxide to a limit of detection below the specification in ISO/DIS 14687-2. The choice of which of these methods to use is therefore likely to depend on which other analytes are also required to be measured, as it is generally beneficially to use as few analytical techniques as possible.

(c) Other candidate methods

Other possible methods for the analysis of carbon monoxide in hydrogen include: GC-MS, CRDS, and FTIR spectroscopy.

4.2.9 Total sulphur compounds

(a) GC-SCD (gas chromatography – sulphur chemiluminescence detection)

Calibration:	Calibration gas mixtures (see Table 3)
Limit of detection:	0.001 µmol/mol
ISO/DIS 14687-2 specification:	0.004 µmol/mol

The analysis of total sulphur compounds to a limit of detection of less than 4 nmol/mol is one of the most challenging specifications given by ISO/DIS 14687-2 due to the issues discussed in Section 3 – sulphur compounds are very unstable at these low concentrations, representative sampling is challenging and the preparation of accurate and traceable calibration gas mixtures for analysis is highly problematic.

To enable the GC-SCD system to be calibrated, four ppb-level calibration mixtures were prepared, two containing hydrogen sulphide in hydrogen, and two containing five sulphur compounds in hydrogen (see Table 3). These mixtures were prepared in 10 litre cylinders with a proprietary internal passivation via a series of dilution from the pure components.

Component	**Amount fraction (µmol/mol)**			
	Mixture (i)	**Mixture (ii)**	**Mixture (iii)**	**Mixture (iv)**
Hydrogen sulphide	0.0200	0.1185	0.0020	0.0038
Carbonyl sulphide	0.0203	-	0.0020	-
Methanethiol	0.0207	-	0.0020	-
Ethanethiol	0.0200	-	0.0020	-
Dimethyl sulphide	0.0201	-	0.0020	-
Hydrogen	balance	balance	balance	balance

Table 3. Calibration gas mixtures prepared at NPL for the measurement of total sulphur compounds presented in this report.

Verification of the mixtures showed that the concentration of hydrogen sulphide in the mixtures was less than expected by gravimetry, but the other components reported analytical concentrations that agreed with the gravimetric values. This loss of hydrogen sulphide, which is unsurprising at these extremely low amount fractions, was accounted for during quantification.

Analysis was carried out using a GC-SCD method with a large (1 ml) sample loop, which enabled the analysis to be carried out without pre-concentration. A GC column with minimum retention properties for sulphur compounds was selected so that all sulphur compounds would be eluted as a single peak, and an isothermal oven temperature of 110°C was used. A dual injection system allowed samples to be injected alternatively from two cylinders (*e.g.* one gas standard and one sample), to enable repeated alternate analyses to take place without having to disconnect the cylinders (and therefore sampling lines) from the system.

Figure 7 shows the repeated alternate analyses of mixture (iii) in Table 3 and a sample of electrolytic hydrogen. Note that because the amount fractions of sulphur compounds are so low the chromatographic peaks are noisy and there is some variance between the peak areas obtained from repeated injections of the same sample – this can only be expected and is taken into account when calculating the uncertainty of the results

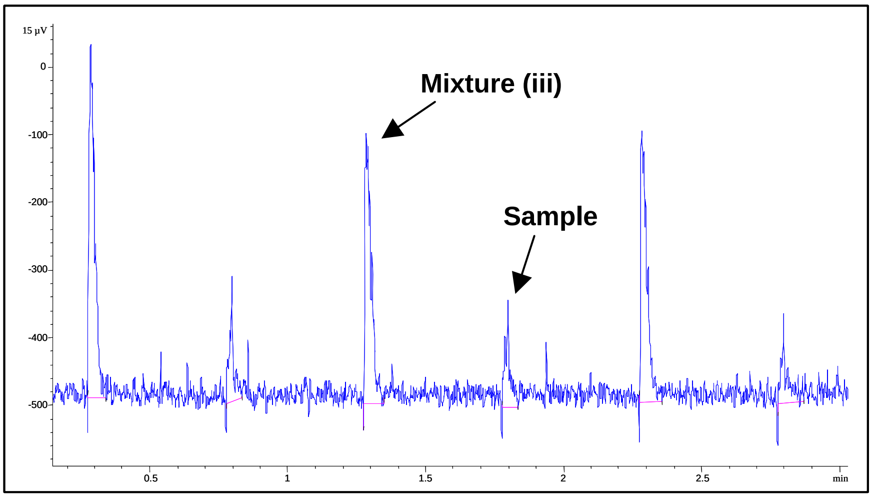


Figure 7. Chromatogram obtained from the GC-SCD analysis of a sample of electrolytic hydrogen. The peaks show the alternate analysis of mixture (iii) in Table 3 and a sample of hydrogen.

The method described above was also used the measure the amount of sulphur compounds present in the following three grades of Air Products commercial hydrogen:

- BIP+ (specified purity: 99.99996 %)
- BIP (specified purity: 99.9992 %)
- Premier Plus (specified purity: 99.95 %)

No sulphur compounds was observed in any of the three cylinders of hydrogen, thus indicating that the amount fraction of total sulphur compounds in each was less than approximately 1 nmol/mol (the limit of detection of the method).

(b) Other candidate methods

Other possible methods for the analysis of sulphur compounds in hydrogen include: GC-AED, GC-PFPD, GC-ECD (operated in sulphur mode), GC-MS, and IC.

4.2.10 Formaldehyde

(a) GC-MS

Calibration: Calibration gas mixture (approx 10 µmol/mol formaldehdye in nitrogen)
Limit of detection: 0.2 µmol/mol
ISO/DIS 14687-2 specification: 0.01 µmol/mol

Figure 8 shows the GC-MS peak obtained from the analysis of the 10 µmol/mol calibration gas mixture using single ion monitoring (*m*/*z* = 30). As is the case with water, calibration gas mixtures containing formaldehyde at lower concentrations are not currently available.

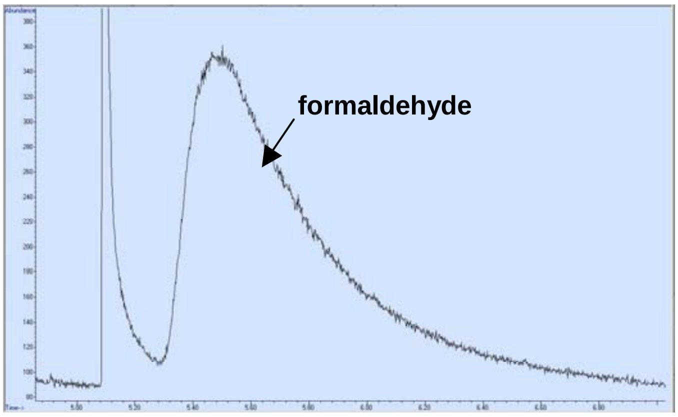


Figure 8. Chromatogram obtained from the GC-MS analysis of a 10 µmol/mol formaldehyde in nitrogen calibration gas mixture, using single ion monitoring mode (*m*/*z* = 30).

Although a distinct peak for formaldehyde is shown in Figure 8, the limit of detection of the method is currently somewhat larger than the ISO/DIS 14687-2 specification and further development is needed. For example, optimisation of the method parameters to improve the peak shape would significantly increase the signal to noise ratio.

(b) Other candidate methods

Other possible methods for the analysis of formaldehyde in hydrogen include: GC-FID, GC-PDHID, CRDS, FTIR spectroscopy, and HPLC.

4.2.11 Formic acid

ISO/DIS 14687-2 specification: 0.2 µmol/mol

A method for the measurement of formic acid in hydrogen has not yet been developed at NPL, but candidate methods to perform this analysis include: GC-MS, GC-FID, GC-PDHID, IC, and CRDS.

4.2.12 Ammonia

(a) GC-MS

Calibration: Calibration gas mixture (approx 10 µmol/mol ammonia in nitrogen)
Limit of detection: 0.5 µmol/mol
ISO/DIS 14687-2 specification: 0.1 µmol/mol

Figure 9 shows the GC-MS peak obtained from the analysis of the 10 µmol/mol calibration gas mixture using single ion monitoring (*m*/*z* = 17). The presence of water in the mixture was confirmed by re-analysing the sample with the mass spectrometer in scan mode, which allowed water to be identified unambiguously.

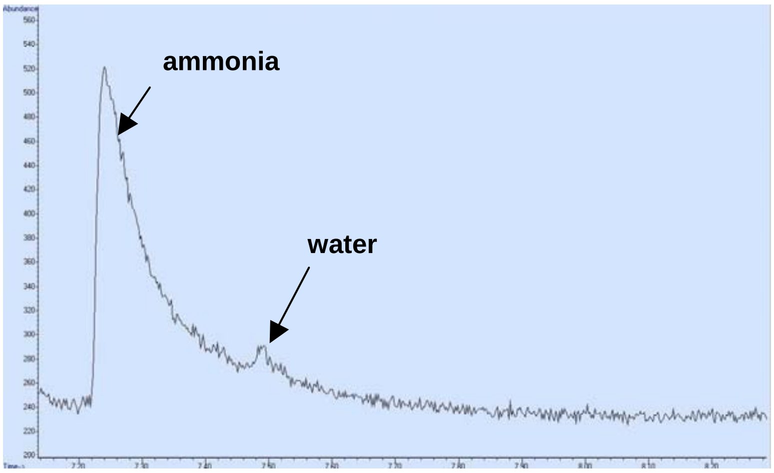


Figure 9. Chromatogram obtained from the GC-MS analysis of a 10 µmol/mol ammonia in nitrogen calibration gas mixture, using single ion monitoring mode (*m*/*z* = 17).

Further method development is expected to enable ammonia to be measured using GC-MS to a limit of detection below the 0.1 µmol/mol specified in ISO/DIS 14687-2.

(c) Other candidate methods

Other possible methods for the analysis of ammonia in hydrogen include: GC-MS, CRDS, FTIR spectroscopy, IC, photo-acoustic IR spectroscopy, and diode laser absorption.

4.2.13 Total halogenated compounds

ISO/DIS 14687-2 specification: 0.05 µmol/mol

A method for the measurement of total halogenated compounds in hydrogen has not yet been developed at NPL, but candidate methods to perform this analysis include: GC-MS, GC-ECD, and IC.

4.2.14 Particulate concentration

ISO/DIS 14687-2 specification: 1 mg/kg

A method for the measurement of particulate concentration in hydrogen has not yet been developed at NPL. The most suitable approach to perform this measurement involves sampling the particulate matter onto a filter, and determining its mass using an accurate gravimetric technique. One such method is described in an ASTM Standard [6].

4.3 SUMMARY OF LIMITS OF DETECTION

The limits of detection of the methods developed in this work and discussed in Section 4.2 are summarised in Table 4:

Component	**ISO/DIS 14687-2 specification (µmol/mol)**	**Method 1**	**Approx. limit of detection (µmol/mol)**	**Method 2**	**Approx. limit of detection (µmol/mol)**
Water	5	CRDS	0.01	GC-MS	0.8
Total hydrocarbon cmpds	2	Meth. GC-FID	0.01	-	-
Oxygen	5	GC-TCD	3	GC-PDHID	0.002
Helium	300	GC-TCD	13	-	-
Nitrogen	100	GC-TCD	8	GC-PDHID	0.003
Argon	100	GC-TCD	5	GC-PDHID	0.01
Carbon dioxide	2	Meth. GC-FID	0.015	GC-PDHID	0.015
Carbon monoxide	0.2	Meth. GC-FID	0.04	GC-PDHID	0.012
Total sulphur compounds	0.004	GC-SCD	0.001	-	-
Formaldehyde	0.01	GC-MS	0.2	-	-
Formic acid	0.2	-	-	-	-
Ammonia	0.1	GC-MS	0.5	-	-
Total halogenated cmpds	0.05	-	-	-	-
Particulate concentration	1 mg/kg	-	-	-	-

Table 4. Summary of limits of detection of the method developed in this work and the ISO/DIS 14687-2 purity specification (Meth. GC-FID = methaniser - GC-FID).

5 ANALYSIS OF ELECTROLYTIC SAMPLES OF HYDROGEN

Example data from the analysis of two sets of samples of hydrogen produced by a number of small-scale electrolytic devices at ITM Power are given for information in Tables 5(a) and 5(b). These are predominantly unpurified samples generated from differential and balanced pressure electrolyser systems. Sample 2 has been passed through an oxygen removal unit prior to sampling.

Component	**Method**	**Measured amount fraction (µmol/mol)**			
		Sample 1	**Sample 2**	**Sample 3**	**Sample 4**
Water	-	-	-	-	-
Total hydrocarbons	Meth. GC-FID	0.541 ± 0.026	0.293 ± 0.046	0.488 ± 0.140	0.503 ± 0.137
Oxygen	GC-TCD	60 ± 12	< 3	81 ± 14	78 ± 14
Helium	GC-TCD	< 13	< 13	< 13	< 13
Nitrogen	GC-TCD	15 ± 5	15 ± 4	< 8	15 ± 4
Argon	GC-TCD	< 5	< 5	< 5	< 5
Carbon dioxide	Meth. GC-FID	0.603 ± 0.051	0.907 ± 0.020	0.720 ± 0.012	3.11 ± 0.05
Carbon monoxide	Meth. GC-FID	< 0.04	< 0.04	0.075 ± 0.023	0.044 ± 0.014
Total sulphur compounds	-	-	-	-	-
Formaldehyde	-	-	-	-	-
Formic acid	-	-	-	-	-
Ammonia	-	-	-	-	-
Total halogenated compounds	-	-	-	-	-
Particulate concentration	-	-	-	-	-

Table 5(a). Results from the analysis of four samples of electrolytic hydrogen (chosen at random) in February 2010. A dash indicates that the measurement was not performed.

Component	**Method**	**Measured amount fraction (µmol/mol)**			
		Sample 5	**Sample 6**	**Sample 7**	**Sample 8**
Water	GC-MS	NQ	NQ	NQ	NQ
Total hydrocarbons	See note (a)	0.53 ± 0.23	0.39 ± 0.07	0.46 ± 0.13	0.31 ± 0.06
Oxygen	GC-PDHID	18.7 ± 3.4	26.8 ± 3.0	40.6 ± 9.9	37.4 ± 3.3
Helium	GC-TCD	< 13	< 13	< 13	< 13
Nitrogen	GC-PDHID	27.3 ± 4.4	37.0 ± 3.9	53 ± 11	44.1 ± 3.9
Argon	GC-TCD	< 5	< 5	< 5	< 5
Carbon dioxide	Meth. GC-FID	1.64 ± 0.17	0.69 ± 0.08	0.38 ± 0.06	2.06 ± 0.22
Carbon monoxide	GC-PDHID	< 0.012	< 0.012	< 0.012	< 0.012
Total sulphur compounds	GC-SCD	< 0.002	0.0025 ± 0.0020	0.0035 ± 0.0020	0.003 ± 0.002
Formaldehyde	GC-MS	< 0.2	< 0.2	< 0.2	< 0.2
Formic acid	-	-	-	-	-
Ammonia	GC-MS	< 0.5	< 0.5	< 0.5	< 0.5
Total halogenated compounds	-	-	-	-	-
Particulate concentration	-	-	-	-	-

Table 5(b). Results from the analysis of four samples of electrolytic hydrogen (chosen at random) in March 2011. A dash indicates that the measurement was not performed; NQ indicates that the amount of water was not quantified as the method was still under development.

Note (a): Non-methane hydrocarbons were measured using methaniser - GC-FID and methane was measured using GC-PDHID. These results were combined to give a result for total hydrocarbons.

The reported uncertainty of each component is the expanded uncertainty (i.e. the standard uncertainty multiplied by a coverage factor of k = 2, providing a level of confidence of approximately 95%). This expanded uncertainty has been calculated by combining all the relevant contributory uncertainty factors, including the repeatability of analysis and the uncertainty in the gas standard or permeation device used to calibrate the instrument. The large uncertainties reported in some cases give an indication of the challenging nature of these analyses at such trace levels.

6 CONCLUSIONS

This report has presented a suite of traceable methods developed for the analysis of key trace-level impurities in hydrogen.

The limits of detection for these methods have been determined and the challenging specifications in current versions of the ISO 14687 draft Standards for hydrogen for the fuel cell industry have been met (and in some cases far exceeded) for: water, total hydrocarbon components, oxygen, helium, nitrogen, argon, carbon dioxide, carbon monoxide and total sulphur components. Methods have also been developed for the analysis of formaldehyde and ammonia, where some further development is required to meet the ISO 14687 specifications.

These analytical methods, which have already been used successfully to measure the levels of impurities in samples of hydrogen generated by small-scale electrolyser devices, will therefore enable industrial users to determine the purity of hydrogen to the necessary accuracy to be suitable for use in fuel cell applications. The methods can also be applied to other industrial applications where purity measurements are critical, for example, the use of hydrogen as a carrier gas in analytical chemistry.

Some work does still remain in this area, however. As well as refining the methods for formaldehyde and ammonia (in parallel with the development of traceable gas standards for these components), methods for the analysis of formic acid, total halogenated compounds and particulate concentration still remain to be developed (if there is a pressing industrial need to do so).

A further challenge is to ensure the analysis of hydrogen for impurities takes place using as few analytical methods as possible. This is essential in order to improve the efficiency of analysis, and also to ensure that analysis can be completed using what may only be a small volume of sample of hydrogen at low pressure. From the work reported here, it can be concluded that GC-PHDID and GC-MS are the two analytical methods most worthy of future effort as these have the potential to perform the simultaneous analysis of many components with low limits of detection.

This work has also developed closer interactions between NPL and key industrial players in hydrogen generation, thus supporting collaborative research projects such as European JTI (Joint Technology Initiative) and the HyQ (Hydrogen fuel Quality requirements for transportation and other energy applications) project. The results of the work are also being disseminated to the Working Groups responsible for developing the International Standards ISO 14687-2 (ISO TC197/WG12) and ISO 14687-3 (ISO TC197/WG14).

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8 ABBREVIATIONS

The following abbreviations and acronyms have been used throughout this report to indicate methods of analysis:

AED	Atomic emission detection
CRDS	Cavity ring-down spectroscopy
PDHID	Pulsed discharge helium ionisation detection
ECD	Electron capture detection
FID	Flame ionisation detection
FTIR	Fourier transform infrared [spectroscopy]
GC	Gas chromatography
HPLC	High-performance liquid chromatography
IC	Ion chromatography
IR	Infrared [spectroscopy]
MS	Mass spectrometry
PFPD	Pulsed-flame photometric detection
SCD	Sulphur chemiluminescence detection
TCD	Thermal conductivity detection

REFERENCES

[1] *UK Government Climate Change Act 2008*. Available online at: www.legislation.gov.uk/ukpga/2008/27/contents (accessed August 2011).

[2] European Commission White Paper COM (2011) 144 final, '*Roadmap to a single European transport area – towards a competitive and resource efficient transport system*'.

[3] ISO/DIS 14687-2 (January 2011 draft international standard version), *Hydrogen fuel — Product specification — Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles*.

[4] ISO/WD 14687-3 (July 2011 working draft version), *Hydrogen fuel — Product specification — Part 3: Proton exchange membrane (PEM) fuel cell applications for stationary appliances.*

[5] ASTM draft work item WK5847 - *Standard practice for sampling of high pressure hydrogen and related fuel cell feed gases.*

[6] ASTM D7651-10 - *Standard test method for gravimetric measurement of particulate concentration of hydrogen fuel.*