Green hydrogen testing
ISO 21087, ISO 14687, EN 17124
PEM Fuel cell applications and risk assessments
Fuel cell electric vehicles are considered to be a very promising alternative to conventional automobiles. They provide zero emissions (only H₂O is produced), high efficiency, long range and short refuelling time. Fuel cell operation relies mainly on platinum catalysts and PEM (proton exchange membrane), both delicate components which are highly sensitive to the quality of the hydrogen fuel.

Various GC & GC-MS methods

International standards ISO 14687 & 21087 address the detailed analysis of impurities in hydrogen. Both standards describe various GC and GC-MS methods for analysing ppb and ppm levels of a range of components. ISO 14687 specifies a restricted list of suggested techniques, while 21087 allows other techniques as well, as long as they are validated. Figure 1 shows an overview of components, maximum allowable levels and GC detectors.

ISO 14687

ISO 14687 describes the following detectors: FID (Flame Ionisation Detector)+methaniser, TCD (Thermal Conductivity Detector), PDD (Pulsed Discharge Detector), SCD (Sulphur Chemiluminescence Detector) and MS (Mass Spectrometer). Components of interest can be pre-concentrated using thermal desorption technique (TD) to obtain lower detection limits. See figure 2, 3 and 4.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Limit 14687 21087 (umol/mol)</th>
<th>Spec. 17124 (umol/mol)</th>
<th>ISO 14687 GC method</th>
<th>ISO 21087 GC method (GAS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total non-hydrogen gases</td>
<td>300</td>
<td>300</td>
<td>TCD, PDD</td>
<td>PDD</td>
</tr>
<tr>
<td>Total hydrocarbons</td>
<td>2 (incl. CH₄)</td>
<td>2 (excl. CH₄)</td>
<td>FID, TD-GCMS</td>
<td>MS*, PDD, FID</td>
</tr>
<tr>
<td>Methane</td>
<td>100</td>
<td></td>
<td>FID</td>
<td>PDD, FID</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5</td>
<td>5</td>
<td>TCD</td>
<td>PDD</td>
</tr>
<tr>
<td>Helium</td>
<td>300</td>
<td>300</td>
<td>TCD</td>
<td>TCD</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>100</td>
<td>300</td>
<td>TCD, PDD</td>
<td>PDD</td>
</tr>
<tr>
<td>Argon</td>
<td>100</td>
<td>300</td>
<td>TCD, PDD</td>
<td>PDD</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>2</td>
<td>2</td>
<td>PDD or methaniser-FID</td>
<td>PDD or methaniser-FID</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>0.2</td>
<td>0.2</td>
<td>PDD or methaniser-FID</td>
<td>PDD or methaniser-FID</td>
</tr>
<tr>
<td>Total sulphur components</td>
<td>0.004</td>
<td>0.004</td>
<td>SCD</td>
<td>MS*</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>0.01</td>
<td>0.2</td>
<td>FID, PDD, TD-GCMS</td>
<td>MS*</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.2</td>
<td>0.2</td>
<td>TD-GCMS</td>
<td>MS*</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
<td>MS* or PDD</td>
</tr>
<tr>
<td>Halogenated components</td>
<td>0.05</td>
<td>0.05</td>
<td>ECD, TD-GCMS</td>
<td>MS*</td>
</tr>
</tbody>
</table>

Figure 1. Impurities, maximum allowable levels and suggested GC detectors according to ISO 14687 & ISO 21087. EN 17124 fuel spec. MS*: ISQ 7000 with AEI (Advanced Electron Ionisation)

Figure 2. Hydrogen purity analyser with dual GC oven, FID, TCD, PDD, mass spectrometer and thermal desorption option.

Figure 3. Low level sulphur analyser with SCD. Limit of detection SCD is < 10 ppb. A pre-concentration device (TD) can be added to increase sensitivity.

Figure 4. Chromatogram SCD. 50 ppm calibration standard.
**ISO 21087**

Figure 5 (see next page) shows the hydrogen purity analyser based on ISO 21087, suggested by GAS. Compared to ISO 14687, it offers (1) lower detection limits, (2) a larger number of analysed components and (3) a less complex analyser configuration. PDD and TCD measure permanent gases, while other components, including ammonia, sulphur components, formic acid, formaldehyde and halogenated compounds, are analysed by MS. The AEI (Advanced Electron Ionisation) source provides detection limits below 0.001 vppm without pre-concentration (TD). Ammonia can be analysed by either MS or PDD, see figure 6, 7, 8, 9 and 10 for chromatograms.

**EN 17124**

EN 17124 specifies quality characteristics of hydrogen fuel and the corresponding quality assurance (see figure 1).

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**Figure 6.** Permanent gases using PDD (10 ppm calibration standard)

**Figure 7.** Halogenated components using mass spectrometer with Advanced Electron Ionisation option

**Figure 8.** $\text{H}_2 \text{S}$ and COS. MS-AEI detection. 2.2 - 56.6 ppb concentration levels (without pre-concentration)

**Figure 9.** Ammonia using Pulsed Discharge Detector. 13.8 ppm calibration standard in $\text{N}_2$. Limit of detection < 100 ppb.

**Figure 10.** Ammonia using mass spectrometer with Advanced Electron Ionisation option
### Specification

**Application:** Hydrogen purity analyser, fuel cell PEM.

**Standardised methods:**
- ISO 14687, ISO 21087, EN 17124
- ISO 14687: GC 1300 with various detectors like TCD, FID (+ methaniser), PDD, SCD, PFPD, MS, Thermal Desorption
- ISO 21087: GC 1300 with MS-AEI (Advanced Electron Ionisation), PDD and TCD

**Options:**
- Stop flow valve
- (Back) pressure regulator
- Heated sample interface
- Selector valves (optionally heated), 4-16 sample inlets or multiple, sequence programmed by Chromeleon datasystem.

**Analysed components:**
- Permanent gases, hydrocarbon, sulphur components, halogenated components, formaldehyde, formic acid, ammonia

**Minimum detectability:**
- Dependant on GC detector:
  - PDD < 50 ppb
  - MS-AEI < 1 ppb
  - TCD < 5 ppm
  - SCD < 10 ppb

**Analysis time:**
- Dependant on used methods

**Sample requirements:**
- See our pre-installation guide

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**Figure 5. Impurities in hydrogen analyser using PDD, TCD and MS-AEI**