Analytical methods for quality control – potentials for cost reduction

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*Hydrogen Fuel Quality Assurance for PEM Fuel Cells – Needs & Status Workshop*

*European Commission, Berlaymont Building, Brussels, Belgium*

*30th September 2014*
Overview of today's presentation

The future...

Hydrogen purity analysis

UK hydrogen energy & recent progress
UK Hydrogen Economy in 2030
A report by UK H2Mobility (2013)

1.6 million fuel cell vehicles on the road in the UK
1,100 hydrogen refuelling stations in operation
254,000 tonnes of hydrogen produced a year
The future…

Fuel cell vehicles – 2015

Hyundai ix35

Nissan X-Trail FCV SUV

Toyota FCV concept

Typical technical specifications for fuel cell vehicles to be available in 2015

<table>
<thead>
<tr>
<th>Vehicle types</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>C/D</td>
<td>Family saloon/estate</td>
</tr>
<tr>
<td>E</td>
<td>Executive</td>
</tr>
<tr>
<td>J</td>
<td>SLV</td>
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<table>
<thead>
<tr>
<th>Commercial introduction</th>
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<tbody>
<tr>
<td>Date</td>
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<table>
<thead>
<tr>
<th>Powertrain</th>
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<tbody>
<tr>
<td>Power source</td>
</tr>
<tr>
<td>Transmission</td>
</tr>
<tr>
<td>Peak power</td>
</tr>
<tr>
<td>Continuous power</td>
</tr>
<tr>
<td>Torque</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressurised hydrogen gas</td>
</tr>
<tr>
<td>Tank pressure</td>
</tr>
<tr>
<td>Capacity</td>
</tr>
<tr>
<td>Consumption (NEDC)</td>
</tr>
<tr>
<td>Range (NEDC)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Performance</th>
</tr>
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<tbody>
<tr>
<td>Top Speed</td>
</tr>
<tr>
<td>Acceleration 0-100km/h</td>
</tr>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Emissions at tailpipe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>NOx (Oxides of Nitrogen)</td>
</tr>
<tr>
<td>Sulphur Dioxide</td>
</tr>
<tr>
<td>Particulates</td>
</tr>
</tbody>
</table>

UK H2 Mobility report (2013)
The future…

UK refuelling stations – 2015-2030

2015-2020
Seeding of Tier 1 regions* – major cities and connecting roads
Initial seeding in major population centres

2020-2025
Coverage extended to Tier 2 and all major roads
Extend coverage to enable close-to-home refuelling to 50% of the population and long distance travel

2025-2030
Full population coverage by 2030
Extend close-to-home refuelling to the whole of the UK, including less populated regions

Vehicle filling
Hydrogen purity
To standard ISO 14687-2
Maximum filled pressure
70MPa (700bar)
Filling time
3 minutes (for a 5kg fill)
Daily capacity
80-1,000kg (i.e. 16-200 full fills)

On-site fuel storage
Pressure
Cascade storage system with highest pressure tank at 85MPa (850bar)
Capacity**
3 days supply

Station size
Daily H₂ capacity
Capacity (FCEV fills/day)
Small
80kg
16
Medium
400kg
80
Large
1,000kg
200

* Tier 1 - LADs with highest spatial density of population and vehicles
* Tier 2 - LADs with intermediate spatial density of population and vehicles
* Tier 3 - LADs with lowest spatial density of population and vehicles

UK H₂ Mobility report (2013)
The proposed EC Directive on the deployment of an alternative fuels infrastructure sets out that:

“Hydrogen refuelling points shall comply with the relevant EN standard, to be adopted by 2014, and, pending publication of this standard, with the technical specifications included in the ISO 14687-2 standard.”

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Amount fraction limit (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>5</td>
</tr>
<tr>
<td>Total hydrocarbons</td>
<td>2</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5</td>
</tr>
<tr>
<td>Helium</td>
<td>300</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>100</td>
</tr>
<tr>
<td>Argon</td>
<td>100</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>2</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>0.2</td>
</tr>
<tr>
<td>Total sulphur compounds</td>
<td>0.004</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>0.01</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.2</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.1</td>
</tr>
<tr>
<td>Total halogenated compounds</td>
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Overview of today's presentation

The future...

Hydrogen purity analysis

UK hydrogen energy & recent progress
Gas chromatography with sulphur chemiluminescence detector

Sulphur Compounds

Water

Helium

Gas chromatography with thermal conductivity detector

Quartz crystal microbalance

Formic acid

Ammonia

Formaldehyde

Under development...

Gas chromatography with mass spectrometer detector (or cavity ringdown spectroscopy)

Water

Helium

Gas chromatography with thermal conductivity detector

Oxygen

Nitrogen

Argon

Gas chromatography with pulsed discharge helium ionisation detector

Hydrocarbons

Gas chromatography with methaniser and flame ionisation detector (backflush capability for hydrocarbons)

Carbon dioxide

Carbon monoxide

Methane

Hydrogen purity analysis
Island Hydrogen (TSB)

“Powering the island using only renewable energy”
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“Powering the island using only renewable energy”

- Wind power
- Electrolysis
- Hydrogen storage
- Power to homes
Island Hydrogen (TSB)

“Powering the island using only renewable energy”
Island Hydrogen (TSB)

“Powering the island using only renewable energy”

Wind power

Electrolysis

Water

Power to homes

Hydrogen

storage

Fuel cell vehicles

Sampling (with sulfinert passivation)

Sampling analysis to recycling

Hydrogen purity analysis

€2k for a sampling vessel

Transport
Unlocking the hydrogen energy market (TSB)

“Develop a low cost online hydrogen purity analyser using cascade laser based systems”

Method validation using traceable offline methods

(only certain impurities can be analysed)
H2FC: Hydrogen to fuel cells

“Reduce costs for full hydrogen purity analysis – by reducing number of analysers”

Limit of detection is too high

Hydrogen purity analysis

Gas chromatography with mass spectrometer

Helium  Water  Hydrocarbons
Formaldehyde  Carbon dioxide  Methane
Formic acid  Carbon monoxide  Sulphur Compounds
Ammonia  Oxygen
Nitrogen  Argon
Halogenated compounds

Impurity enrichment
**H2FC: Hydrogen to fuel cells**

- Allows measurement of lower amount fractions
- Better signal-to-noise
- Can be used with any analyser
- Offline or online enrichment

Gas Sampling and Impurity Enrichment Device (GSIED)

Argonne National Lab’s enrichment method
Hydrogen purity analysis

**H2FC: Hydrogen to fuel cells**

Hydrogen sample

Krypton (Tracer)

Combine

Measure krypton

Hydrogen removal

Measure impurities

Measure krypton

Enrichment factor

**Hydrogen Impurity Enrichment Device (HIED)**

NPL’s tracer enrichment method
Hydrogen purity analysis

H2FC: Hydrogen to fuel cells

Paper published in Royal Society of Chemistry’s Analytical Methods journal

Selected as a HOT article by RSC

To be included in a special issue of the journal: ‘Emerging analytical methods for global energy and climate issues’

Advancing the analysis of impurities in hydrogen by use of a novel tracer enrichment method

H2FC: Hydrogen to fuel cells

One of many conclusions:

Device works well, but further work required with regards to the improvement of palladium-based membranes…
NPL Innovation Research & Development Project

“Develop a suite of characterisation tools to help improve palladium-based membranes”
Overview of today's presentation

The future...

Hydrogen purity analysis
Hydrogen purity in the future

- Hydrogen refuelling station
- Sampling
- Transport
- Hydrogen purity laboratory (non-NMI)
- Online analyser
- Enrichment
- Sampling
- Transport
- Purity analysis
The future…

Hydrogen purity in the future

- Offline analysis
  - Full range of analytes
  - High accuracy
  - Limited range of detection
  - Long analysis time
  - Delayed results
  - High cost

- Online analysis
  - Immediate analysis
  - Low cost
  - Minimal labour required
  - Limited analytes
  - Limited range of detection
  - One required at each station

- Offline analysis with enrichment
  - Full range of analytes
  - Low cost
  - Improved range of detection
  - Long analysis time
  - Delayed results
  - Problems with reactive species
The future…

Hydrogen purity in the future

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Current hydrogen purity specifications (ISO 14687-2)

The next steps for hydrogen purity

- New European standard for $\text{H}_2$ purity (2016)
- Further development of traceable offline methods
- Hydrogen impurity enrichment device
- Develop the online purity analyser