

## New methods for hydrogen purity analysis

The future uptake of hydrogen as a fuel is crucially dependent on the availability of hydrogen of sufficient purity, since impurities at even trace levels can severely affect the performance of fuel cells. These purity requirements are being set out in the draft International Standards ISO/DIS 14687-2 and ISO/WD 14687-3.

In order to meet this pressing industrial need for accurate and traceable hydrogen purity analyses, the UK's [National Physical Laboratory](#) (NPL) has developed a suite of analysis methods in a collaborative project with [ITM Power](#), [Air Products](#) and the [UK Hydrogen and Fuel Cell Association](#).

### Analytical challenges

The challenges successfully overcome during the development of these methods include:

- Achieving the highly challenging (low ppb-level) specifications for key components.
- Developing methods for reactive and non-stable components (*e.g.* sulphur species and formaldehyde) by the use of passivated sampling vessels and analytical devices.
- Overcoming the lack of traceability for some analyses – stable gaseous reference materials are not currently available for a number of components.
- Avoiding air contamination (crucial for the measurement of oxygen and nitrogen).
- Ensuring that a representative sampling method is used to take samples of hydrogen into cylinders for laboratory analysis.

### Methods developed

The analytical methods developed at NPL are summarised in the table below. Work to develop methods for other components (*e.g.* formic acid and halogenated compounds) is on-going.

Component	ISO/DIS 14687-2 specification † (µmol/mol)	NPL method limit of detection (µmol/mol)	NPL methods developed (The stated limit of detection applies to the first method listed)
Water	5	0.01	CRDS, GC-MS
Total hydrocarbons	2	0.01	Methaniser GC-FID
Oxygen	5	0.002	GC-PDHID, GC-TCD
Helium	300	13	GC-TCD
Nitrogen	100	0.003	GC-PDHID, GC-TCD
Argon	100	0.01	GC-PDHID, GC-TCD
Carbon dioxide	2	0.015	GC-PDHID, methaniser GC-FID
Carbon monoxide	0.2	0.012	GC-PDHID, methaniser GC-FID
Total sulphur compounds	0.004	0.001	GC-SCD
Formaldehyde	0.01	0.2	GC-MS
Ammonia	0.1	0.5	GC-MS

† Specification taken from the draft of ISO/DIS 14687-2 dated January 2011.

## Case study – total sulphur compounds

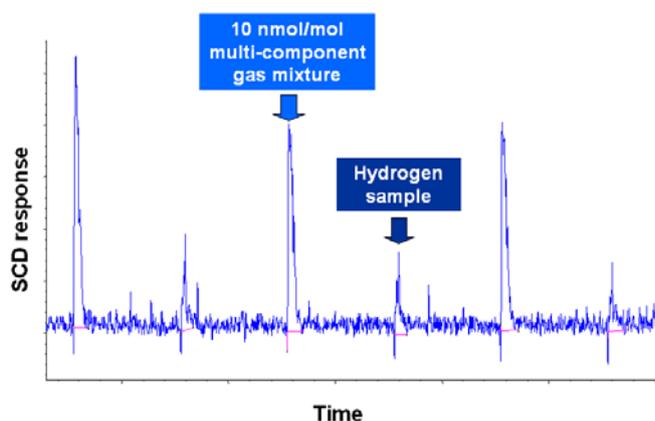
The analysis of total sulphur compounds to a limit of detection of less than 4 nmol/mol is one of the most challenging specifications given by ISO/DIS 14687-2 due to the issues highlighted previously - sulphur compounds are very unstable at these very low concentrations, representative sampling is challenging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

To perform these measurements, a new GC-SCD (gas chromatography – sulphur chemiluminescence detection) method has been developed at NPL using a GC column with minimal retention, so that all sulphur compounds of interest are eluted as a single GC peak. The use of a large sample loop allows the challenging limit of detection to be achieved without the need for pre-concentration of the sample.

To enable the GC-SCD system to be calibrated, a series of ppb-level standard gas mixtures have been developed, containing up to five sulphur compounds in hydrogen. A dual injection system allows samples to be injected alternatively from two cylinders to enable repeated alternate analyses to take place without having to disconnect the cylinders (and therefore sampling lines) from the system.

The chromatogram below shows the repeated alternate analyses of:

- (a) A standard gas mixture containing 2 nmol/mol of each of five sulphur compounds (hydrogen sulphide, carbonyl sulphide, methanethiol, ethanethiol and dimethyl sulphide) in hydrogen.
- (b) A sample of electrolytic hydrogen.



The five sulphur compounds with a total amount fraction of 10 nmol/mol can be clearly seen as a single (non-separated) peak. The noisy chromatographic peaks are a consequence of the very low concentrations of sulphur components being measured.

## Further information

Full details of work carried out to develop these methods for hydrogen purity analysis are available in NPL Report AS 64 - *Methods for the analysis of trace-level impurities in hydrogen for fuel cell applications* - which is available for [free download](#) from the NPL website.

For further information, including details of NPL's hydrogen purity analysis services, please contact Dr Andrew Brown: [andrew.brown@npl.co.uk](mailto:andrew.brown@npl.co.uk) / +44 20 8943 6831.