



A novel method for measuring trace amounts of total sulphur-containing compounds in hydrogen



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ABSTRACT

A novel method for the analysis of total sulphur-containing impurities in a hydrogen matrix has been developed. This method has a limit of detection (LoD) significantly lower than that maximum amount fraction for sulphur-containing compounds (4 nmol mol^{-1}) specified by the international standard for hydrogen to be used in fuel cell vehicles (ISO 14687-2). To measure the LoD for this method, a novel gas standard containing five different sulphur-containing compounds at low nmol mol^{-1} amount fractions has been gravimetrically prepared. Stable primary gas standards that are traceable to the SI were used to successfully validate the amount fractions of the sulphur-containing compounds in this gas standards using gas chromatography with flame ionisation detection (GC-FID) and sulphur chemiluminescence detection (GC-SCD).

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1. Introduction

As Governments set targets to reduce carbon dioxide emissions and increase the use of energy produced from renewable sources [1,2], several new energy infrastructures are becoming established. To realise these targets, powering vehicles using hydrogen is one possible route.

Hydrogen is predicted to be a key future energy vector as it can be produced by a completely carbon free path at the point-of-use; one way being to use electrolysis powered by renewable energy sources [3]. Additionally, the use of proton exchange membrane (PEM) fuel cells in vehicles or other devices is a viable method for providing energy to these systems without releasing carbon dioxide or other pollutants into the urban environment. These qualities have led major automotive manufacturers to produce hydrogen fuel cell vehicles and several countries to establish hydrogen refuelling networks: as of March 2013 there were 208 hydrogen re-fuelling stations worldwide with 95 more planned [4,5].

PEM fuel cells operate by facilitating the catalytic reaction of hydrogen with oxygen from the air across an electrolyte that is permeable only to hydrogen ions, thus producing an electric current. A significant potential drawback is that the catalyst (usually platinum) used at the fuel cell cathode is very susceptible to

degradation by impurities. Therefore in order to ensure fuel cell lifetime, the hydrogen supplied to the device must meet stringent purity requirements.

In order to address this issue, standards have been published that dictate the minimum quality of hydrogen that should be used in fuel cell vehicles. A recent ISO (International Organisation for Standardisation) standard (ISO 14687-2) [6] provides purity specifications for hydrogen to be used in PEM fuel cells (Table 1). The SAE (Society of Automotive Engineers) have used the same purity criteria in their own standard SAE J2719 [7]. Future legislation is likely to incorporate these specifications, as indicated by the proposed EC Directive [8] on the deployment of an alternative fuels infrastructure which states, “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 14687-2:2012 standard.”

This paper discusses the analysis of total sulphur-containing compounds in hydrogen with the aim of achieving a limit of detection (LoD) lower than the maximum allowed amount fraction specified in ISO 14687-2 (4 nmol mol^{-1}) (the standard also has an additional, non-mandatory recommendation that the LoD should ideally be three times lower than this).

Sulphur-containing compounds can be present in hydrogen produced by the steam reformation of natural gas [6]. The typical compounds found are likely to be those originally present in natural gas such as thiols, organic sulphides and hydrogen sulphide. The analysis of such compounds in odourised natural gas is well

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Table 1
Maximum impurity levels that should not be exceeded for PEM fuel cell hydrogen as specified by ISO 14687-2.

Impurity	Maximum amount fraction ($\mu\text{mol mol}^{-1}$)
Water	5
Total hydrocarbons	2
Oxygen	5
Helium	300
Nitrogen	100
Argon	100
Carbon dioxide	2
Carbon monoxide	0.2
Total sulphur compounds	0.004
Formaldehyde	0.01
Formic acid	0.2
Ammonia	0.1
Total halogenated compounds	0.05

established [9] however, this generally concerns the analysis of individual components at the parts-per-million ($\mu\text{mol mol}^{-1}$) level and not the more challenging analysis of total sulphur-containing compounds at the parts-per-billion (nmol mol^{-1}) levels as discussed in this paper.

ISO 14687-2 also gives examples of analytical techniques for the measurement of the impurities highlighted in Table 1. For the analysis of sulphur-containing compounds three different methods are described, one using gas chromatography with a sulphur chemiluminescence detector (GC-SCD) and a pre-concentration device, the second using flame decomposition followed by oxidation and analysis using ion chromatography with a concentration device. The third method is an earlier version of that described in this paper which uses GC-SCD without any concentration device [10]. An ASTM standard [11] also exists that describes a method of total sulphur analysis using a cryogenic pre-concentrator and GC-SCD analysis. Several reports and papers discuss the validation of the analytical methods listed in ISO 14687-2 and further work has suggested alternative approaches [12,13].

There are two major problems with some of the methods currently suggested for the analysis of total sulphur-containing compounds. First, most do not actually measure all of the sulphur-containing compounds together, but rather measure the amount fraction of the individual compounds and then sum these for the total sulphur content. Any method such as this can lead to erroneous statements of compliance with the specifications as the individual compounds can be below the LoD when measured separately but may exceed the required quality limits when combined. Secondly, the majority of the methods currently employed use some form of pre-concentration of the sulphur-containing compounds. Due to the potential for chemisorption, this should be avoided as the sulphur-containing compounds are likely to become permanently bound to any pre-concentration device and again, this would likely result in false negatives being reported.

This paper describes a novel method for measuring parts-per-billion (nmol mol^{-1}) levels of total sulphur-containing compounds in hydrogen by using GC-SCD without the need for pre-concentration. The method, which has been validated by the analysis of gas standards traceable to primary national standards, provides a rapid solution for this highly challenging measurement. Additional novelty is provided by the gas standards used in the study, as standards of sulphur-containing compounds have not previously been prepared and validated at the amount fractions described here.

The SCD was identified as the most suitable detector for the work as it has a very low LoD, in the parts-per-trillion range (pmol mol^{-1}) [14], and it exclusively detects sulphur-containing compounds. The SCD works in such a way that it is effectively a sulphur atom

counter, producing a signal proportional to the number of sulphur atoms in a compound. This means, for instance, one molecule of diethyl disulphide gives a peak area twice that of one molecule of diethyl sulphide.

The analysis used a novel peak combination method, measuring all of the compounds as one total analyte peak rather than individual peaks for each compounds. In addition to measuring the sulphur-containing compounds as a total, combining the compounds into one analyte peak also gives a lower LoD relative to the total sulphur content and more repeatable peak areas, as the combined peak is larger than the individual peaks.

The LoD of the method was determined using a novel gas standard which was prepared containing five different sulphur-containing compounds each at nominally 20 nmol mol^{-1} in hydrogen. This amount fraction was chosen due to concerns about the stability of mixtures of lower amount fractions, caused by adsorption of the molecules to the internal surfaces of the cylinder. This standard was then validated by analytical comparison against other gas standards traceable to the International System of Units (SI).

2. Materials and methods

2.1. Gas standards preparation

Seven gas standards were prepared in accordance with ISO 6142 [15] using high purity hydrogen (purity grades N6.0 and BIP+), nitrogen, propane (Air Products, UK), ethanethiol, ethylmethyl sulphide, diethyl sulphide (Acros Organics, UK), methanethiol, dimethyl sulphide, carbonyl sulphide (Sigma–Aldrich, UK) and hydrogen sulphide (BOC, UK). The components used were typically of the highest purity commercially available and purity analysis was performed to identify and quantify any impurities present. The preparation scheme is illustrated in Fig. 1.

The compositions of the seven gas standards are given in Table 2. Each mixture was prepared in a 10L (internal water volume) aluminium cylinder (BOC, UK) with an NPL-designed DIN 477 No.1 outlet diaphragm valve (Rotarex Ceodeux, Luxembourg), with an internal screw thread to minimise dead volume. The cylinders were treated using the BOC ‘Spectraseal’ process designed to render the internal aluminium surfaces chemically inert and thus minimise the adsorption of compounds to the cylinder walls. Prior to use, the cylinders were evacuated to 1.5×10^{-7} mbar using a turbo molecular pump (Leybold Vacuum, UK) then conditioned prior to use using a NPL proprietary treatment.

The compounds were added to the cylinder being filled either by direct transfer via a length of 1/16 inch external diameter stainless steel tubing (Swagelok, UK) that had been internally passivated using the Silcosteel® process (Thames Restek, UK), or by using an intermediate vessel constructed of stainless steel.

Upon completion of preparation, the mixtures were homogenised by heating the cylinder in an inverted position at approximately 60°C for 2 h, followed by rolling along the vertical axis for 2 h. The composition of the mixtures (amount fraction and associated uncertainty of each compound) were calculated using the software package ‘GravCalc2’ [16] (NPL, Teddington, UK).

2.2. Analysis

All of the analysis performed takes into account any sampling issues associated with low amount fractions of sulphur compounds, as highlighted by Brown et al. [17]. The analysis was performed on an Agilent 7890 GC equipped with an SCD and a flame ionisation detector (FID). The gas standards were connected to the GC via minimum dead volume flow metering valves, all parts of

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