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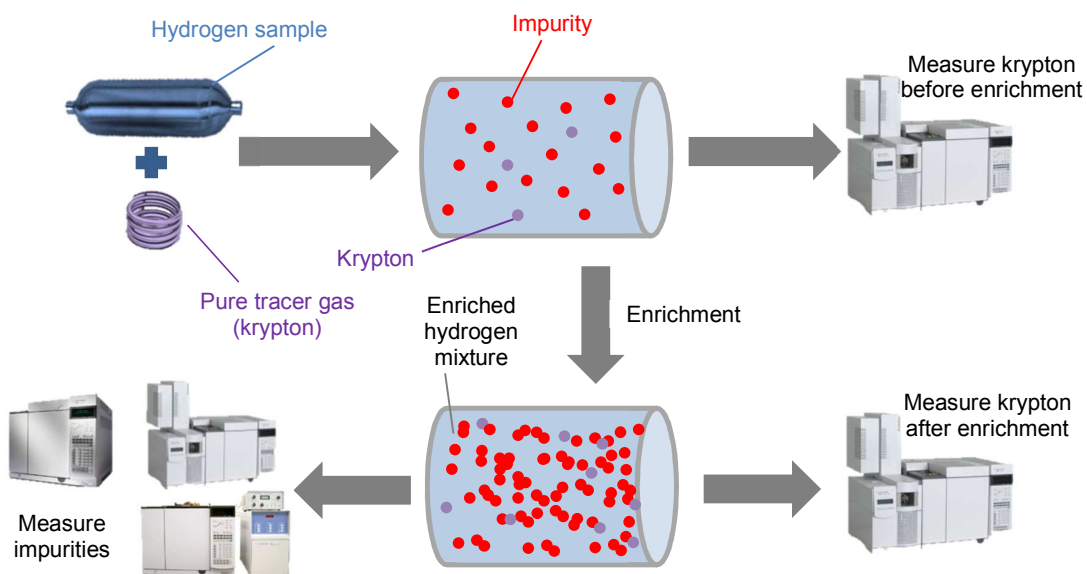
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This paper presents and validates a novel hydrogen impurity enrichment method that can be used for concentrating the impurities in hydrogen to facilitate more routine and cost-effective purity analysis of fuel cell hydrogen



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

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A novel tracer enrichment method for concentrating the impurities in hydrogen has been developed and validated. The method calculates the enrichment factor by spiking the gas mixture with krypton and measuring the change in amount fraction before and after enrichment. This method was compared against an existing non-ideal gas law enrichment method which calculates the enrichment factor by measuring the change in pressure and temperature of the hydrogen gas mixture. The comparison was achieved by performing tests where both methods were successfully used to calculate the amount fractions of nitrogen, carbon monoxide and methane in a mixture of hydrogen with a known composition. An uncertainty budget for both methods was also developed showing that the new tracer enrichment method gives a lower uncertainty of measurement compared to the non-ideal gas law enrichment method. An additional benefit to using the tracer enrichment method is that accurate measurements can be performed even during an air leak or membrane failure. It was concluded that a combination of both of the two enrichment techniques would form the ideal measurement tool for performing accurate measurement of impurities while being able to detect leaks and monitor the enrichment factor.

## 1. Introduction

With increasing requirements to limit, control and reduce greenhouse gas emissions, hydrogen is globally recognised as a suitable energy vector for powering vehicles (and other small devices). Hydrogen can be employed to power vehicles either by using an internal combustion engine or fuel cell; both of these routes provide clean energy with no carbon emissions (if produced from a renewable source) by reacting the hydrogen with oxygen from the air. Whereas the internal combustion engine is relatively robust in terms of the proportion of impurities that can be present in the fuel, hydrogen fuel cells require very high purity grades of hydrogen in order to prevent deactivation of the catalyst, which would lead to reduced fuel cell lifetime.

Various studies<sup>1,2</sup> have been performed that have specifically investigated the effects of hydrogen impurities on fuel cell lifetime, and more recently the international standard ISO 14687-2:2012 has been published, which provides a list of the maximum levels of impurities that can be present in hydrogen for proton exchange membrane (PEM) fuel cell vehicles (Table 1).<sup>3</sup> The proposed EC Directive on the deployment of an alternative fuels infrastructure<sup>4</sup> 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 14687-2:2012 standard.” If hydrogen is therefore to be used as an energy vector for commercial fuel cell vehicles, it is essential that reliable measurements of the purity of hydrogen are available.

**Table 1** Maximum impurity levels that should not be exceeded for PEM fuel cell hydrogen as specified by ISO 14687-2:2012

| 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             | 0.1  |
| Total sulphur compounds     | 0.004  |
| Formaldehyde                | 0.01   |
| Formic acid                 | 0.2  |
| Ammonia                     | 0.1  |
| Total halogenated compounds | 0.05   |

Although the standard does also include particulates (at a maximum level of  $1 \text{ mg kg}^{-1}$ ), for the purpose of this paper Table 1 only lists the gaseous impurities specified by the standard. As some impurities such as the reactive components (e.g. sulphur compounds and formaldehyde) are much more detrimental to fuel cells compared to other inert components (e.g. helium and nitrogen), these impurities are specified with a challengingly low maximum allowable levels.

The requirement for having to measure several impurities at very low amount fractions makes purity analysis a difficult task. Not only does this require several high performance gas

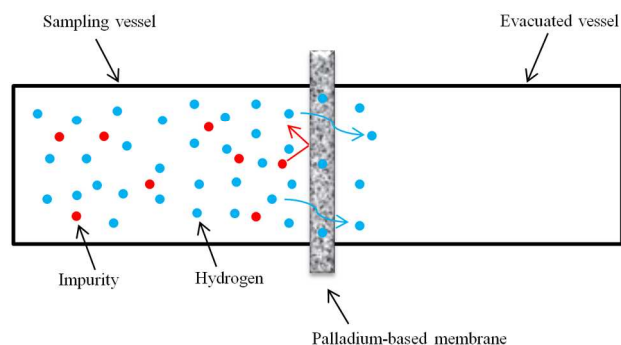
analysers,<sup>5</sup> in some cases the amount fraction of an impurity that would need to be measured may be close to or below the limit of detection of the analyser. If the impurities in the gas were enriched by a known factor this would increase the concentrations of the impurities to levels above the limits of detection, facilitating more routine and accurate analysis.

An enrichment method using a palladium-based membrane has previously been developed by Papadias *et al.* at the Argonne National Laboratory.<sup>6</sup> In this system, a mixture of impure hydrogen is contained in a vessel and pure hydrogen is extracted out through a palladium-based membrane leaving the impurities behind (Figure 1). By measuring the changes in pressure and temperature of the gas, the reduction in the amount of hydrogen can be calculated using the non-ideal gas law (equation 1) and this is used to determine a calculated enrichment factor (CEF) as detailed in Section 2.

$$n = \frac{PV}{ZRT} \quad (1)$$

Where  $n$  is the amount of gas,  $P$  is pressure,  $V$  is volume,  $Z$  is compressibility factor,  $R$  is the gas constant and  $T$  is temperature.

The amount fractions of the impurities in the enriched gas mixture are then measured on a gas analyser and using the CEF the original amount fractions of the impurities can be determined. The methodology and principles behind this process are discussed in more detail in Section 2.



**Fig. 1** Principle of the hydrogen impurity enrichment method.

Papadias *et al.* validated the impurity enrichment method by measuring a known gas standard of hydrogen containing a volume fractions of  $\sim 2 \text{ mL L}^{-1}$  nitrogen, methane, carbon monoxide and carbon dioxide, the results from which indicated a difference between calculated and measured enrichment factor of less than 3%. In all of the tests the nitrogen amount fraction was always higher than expected, whereas for methane, carbon monoxide and carbon dioxide the amount fractions were lower than expected. In a further test the enrichment method was validated using a known gas standard containing hydrogen sulphide, nitrogen, methane, carbon monoxide and carbon dioxide in hydrogen. The results from this test indicated that there was a loss of hydrogen sulphide during the enrichment process, which lead to a lower enrichment factor compared to the CEF. It

was suspected that the hydrogen sulphide had either reacted or adsorbed onto the membrane.

A similar device called a hydrogen elimination mass spectrometer, has been developed by Bossard *et al.* who have integrated a palladium-based membrane directly into a mass spectrometer.<sup>7</sup> In this system the impurities are measured by mass spectrometry in selected ion monitoring mode following enrichment. A feature that this system also incorporates is the ability to flow pure hydrogen (produced during the enrichment stage) back into the sampling vessel which can then be used to determine if any of the impurities remain in the vessel. This could be particularly important for adsorptive components such as hydrogen sulphide.

An aspect of both of the enrichment processes that needs to be investigated in more detail is the uncertainty of the measurements obtained. In order to properly assess this, all of the uncertainty contributions involved in calculating the enrichment factor (including any measurements of pressure, volume and temperature) must be determined and quantified. Determination of the total uncertainty would provide essential information regarding the comparability of the measurements.

Whereas the two enrichment methods discussed above have calculated the enrichment factor using the non-ideal gas law, this paper presents and validates a novel 'tracer enrichment method' where the enrichment factor is calculated by accurately measuring the change in the amount fraction of a spiked component (krypton) before and after enrichment, thus eliminating any uncertainties from physical measurements (such as pressure, temperature and volume from the calculation). The results from this enrichment method are compared to the non-ideal gas law enrichment method devised by Papadias *et al.* A full assessment of the uncertainties for both enrichment methods is undertaken.

## 2. Theory

### 2.1 Principles of hydrogen impurity enrichment

#### 2.1.1 Non-ideal gas law enrichment method

The non-ideal gas law enrichment method utilises a palladium-copper coated palladium-silver alloy membrane to enrich impurities in a sample of hydrogen. The experimental set-up for this method at NPL is shown in Figure 2. The hydrogen gas mixture is filled into two evacuated vessels (V1 and V2) where the second vessel (V2) holds the palladium-based membrane and the valve separating the two vessels (NV2) is closed. The pressures and temperatures of both vessels are measured initially before enrichment. V2 is heated to above 300 °C to activate the membrane, allowing pure hydrogen to permeate out through the palladium membrane. Following a reduction in pressure in V2, NV2 is re-opened to introduce more hydrogen from V1. It is important to note that there must be no back-flow of hydrogen from V2 to V1 as this would invalidate the enrichment factor calculation. Also the pressure in V2 must not exceed 20 bar as this can cause damage to the membrane. Following suitable enrichment of the impurities (to levels that can be measured repeatedly on the intended gas analyser), the pressures and temperatures of both vessels are measured again.

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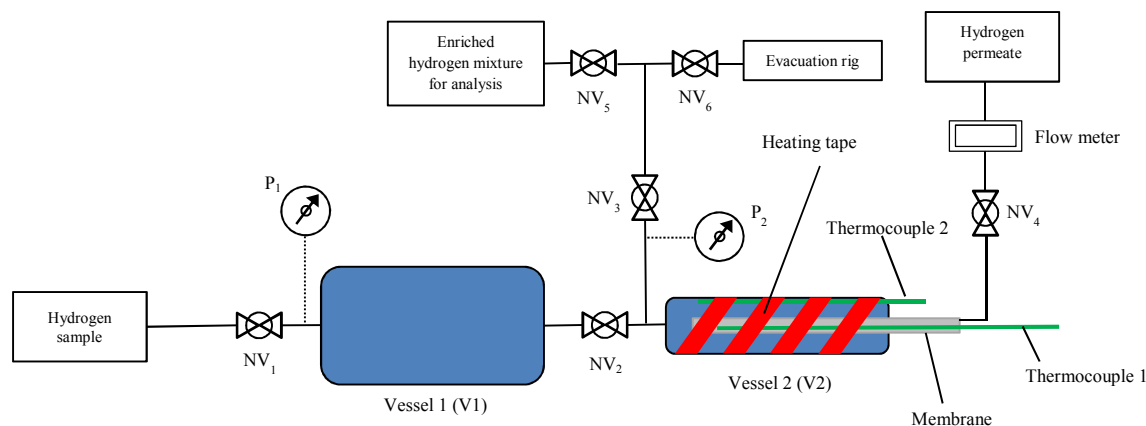


Fig. 2 Schematic diagram of the hydrogen impurity enrichment device used at NPL

As described by Papadias *et al.*<sup>6</sup> a molar balance of the impurities in the system before and after enrichment can be performed to obtain the following equation:

$$y_{1,a}n_{1,a} + y_{1,a}n_{2,a} = y_{1,b}n_{1,b} + y_{1,b}n_{2,b} \quad (2)$$

where  $y_{1,a}$  is the amount fraction of the impurity before enrichment,  $y_{1,b}$  is the amount fraction of the impurity after enrichment and  $n$  is the amount of gas in either of V1 and V2 in stage a (before enrichment) or stage b (after enrichment).

By rearranging this equation, the calculated enrichment factor (CEF) can be determined:

$$CEF = \frac{y_{1,b}}{y_{1,a}} = \frac{n_{1,a} + n_{2,a} - n_{1,b}}{n_{2,b}} \quad (3)$$

By substituting in the non-ideal gas law into equation (3), the following can be obtained:

$$CEF = \frac{\left(\frac{P_{1,a}V_1}{Z_{1,a}RT_{1,a}}\right) + \left(\frac{P_{2,a}V_2}{Z_{2,a}RT_{2,a}}\right) - \left(\frac{P_{1,b}V_1}{Z_{1,b}RT_{1,b}}\right)}{\left(\frac{P_{2,b}V_2}{Z_{2,b}RT_{2,b}}\right)} \quad (4)$$

Therefore by determining the pressures, volumes, compressibility factors and temperatures before and after enrichment, these values can be substituted into equation (4) to determine the CEF. Once the CEF is calculated, the amount fraction of the enriched impurity ( $y_{1,b}$ ) can be measured by opening NV3 and NV5, and

analysing the outlet gas. This value along with the CEF can be substituted into equation (3) to solve for  $y_{1,a}$  (the original amount fraction of the impurity). More detailed information on the non-ideal gas law enrichment method can be found in the paper of Papadias *et al.*<sup>6</sup>

### 2.1.2 Tracer enrichment method

The non-ideal gas law enrichment method described in Section 2.1.1 uses the measurement of various physical properties such as pressure, temperature and volume to calculate the CEF, and because there are a number of variables (each with a contributing uncertainty), one might expect a large overall uncertainty for the CEF. One strategy for reducing this uncertainty would be to minimise the number of variables in equation (4) or to use a method with different variables that would contribute less uncertainty. The novel tracer enrichment method described in this paper eliminates the need for measurement of physical properties to determine the CEF by introducing an inert gas into the sample before enrichment. The amount fraction of tracer gas is analysed immediately before enrichment and again following enrichment to determine the CEF (Figure 3).

The component selected as a tracer must not be expected to be present in the sample and, most importantly, it must be an inert gas so as not to adsorb or react in the sampling vessel under high temperatures or in the presence of the palladium-based membrane. Krypton and neon are suitable tracers that meet these criteria.



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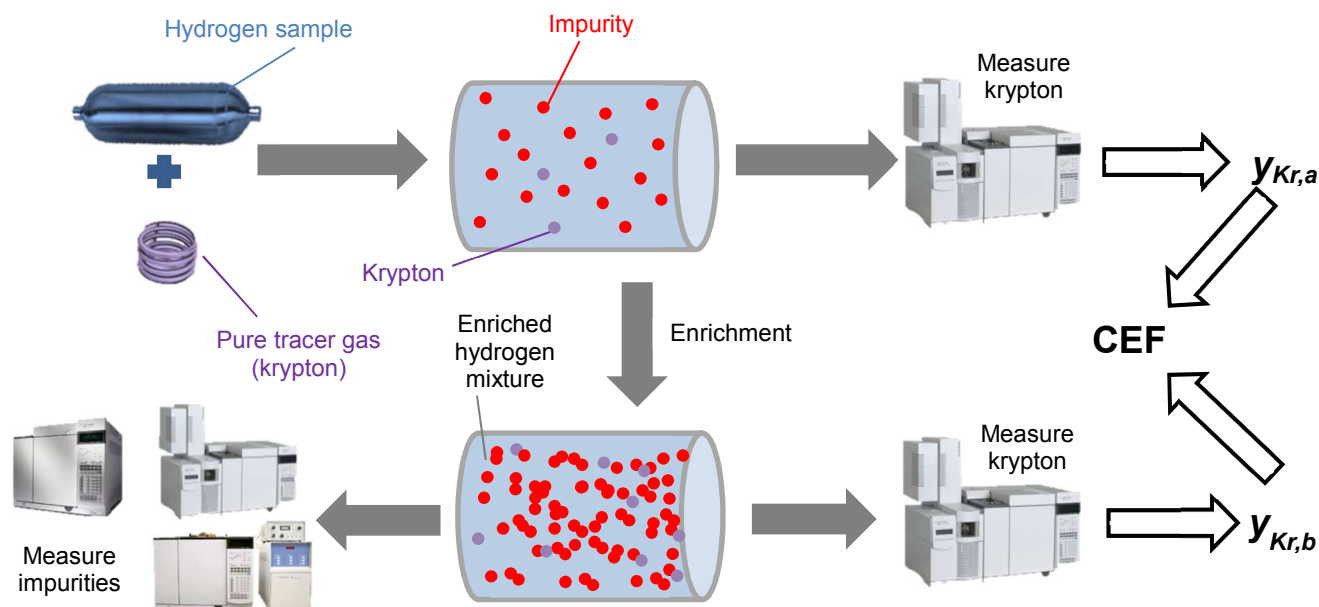


Fig. 3 Schematic diagram of the tracer enrichment method

The equation for determining CEF using the tracer enrichment method can be expressed by:

$$CEF = \frac{y_{Kr,b}}{y_{Kr,a}} = \frac{1}{y_{Kr,a}} \frac{A_{Kr,b}}{A_{Kr,st}} b y_{Kr,st} \quad (5)$$

where  $y_{Kr,a}$  is the amount fraction of krypton in the unenriched gas mixture,  $y_{Kr,b}$  is the amount fraction of krypton in the enriched gas mixture,  $y_{Kr,st}$  is the amount fraction of krypton in the calibration standard (used to calibrate the analyser),  $A_{Kr,b}$  is the response measured on the analyser for krypton after enrichment,  $A_{Kr,st}$  is the response measured on the analyser for the krypton in the calibration standard and  $b$  is a correction factor for the linearity of the detector. In this work  $b$  was set to 1 but the term has been included in equation (5) to allow a component of uncertainty for this term to be included in the uncertainty budget.

Using this alternative approach to determine the CEF, each term in equation (5) may have a small associated uncertainty if the calibration standard is prepared to a high accuracy and the analyser can provide repeatable results. National Measurement Institutes such as the National Physical Laboratory can provide highly accurate and traceable primary reference gas standards using gravimetric preparation techniques which ensure that the relative uncertainty of the amount fractions of the components in the calibration gas standard are often less than 0.2%.<sup>8</sup> Gas analysers such as gas chromatography with pulsed discharge helium ionisation (GC-PDHID) or mass spectrometry (GC-MS) detectors can be used to measure multiple impurities in one

method with low standard deviations for the measurements.

When using membranes to perform impurity enrichment, there are certain unavoidable circumstances that would affect the enrichment measurement. This could include:

- 1) failure of the membrane producing a leak,
- 2) air leaks into the enrichment vessels,
- 3) back-flow of gas from V2 into V1.

Membrane failure can be a common occurrence when operating systems at high temperatures and pressures due to the applied stress that is subjected to the membrane as it expands and contracts. Air leaks may also occur due to expansion of the vessel connections at high temperatures.

All three of the issues listed would affect the CEF calculated by the non-ideal gas law enrichment method and, importantly, there would be no indication that any of these issues had occurred simply by examining the experimental data. However, for the tracer enrichment method, none of these issues would affect the CEF calculation because the amount fraction of tracer in the gas mixture will be affected in an identical way to the impurities (covariance). This essentially means that any external effects that are applied to the impurities (such as loss of impurities through membrane cracks or dilution of impurities by air) would also be subjected to the tracer compounds in the same manner, allowing the CEF to still be calculated. The only components that would not be accurately determined are nitrogen and oxygen during an air leak.

In addition to not being affected by leaks, the CEF for the tracer enrichment method is based on a change in amount fraction of the tracer compound and therefore it is also not affected if gas accidentally flows back from V2 into V1.

### 3. Material and methods

#### 3.1 Equipment

##### 3.1.1 Hydrogen impurity enrichment device

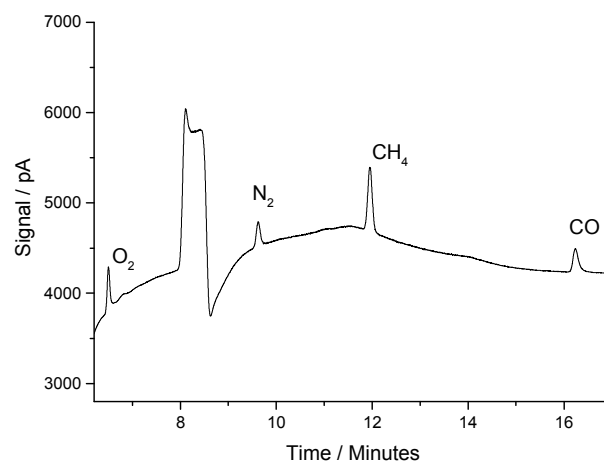
The experimental set-up for performing hydrogen impurity enrichment is based on the work performed by Papadias *et al.*<sup>6</sup> and a schematic is shown in Figure 2. The set-up comprises of two Sulfinert®-treated sampling vessels (Thames Restek, UK) with nominal volumes of 1000 cm<sup>3</sup> (V1) and 300 cm<sup>3</sup> (V2). A palladium-silver alloy coated with palladium-copper (REB Research & Consulting, USA) was selected as a suitable membrane for performing enrichment of impurities in hydrogen whilst preventing adsorption of reactive components. The membrane was attached inside V2 so that the majority of the membrane sat inside the vessel and one end was connected to a flow meter to allow the flowrate of the permeated hydrogen to be monitored and vented. Heating tape and a controller (Omega Engineering Limited, UK) was used to heat the outside of V2 to allow the membrane inside to reach 300 °C. Two thermocouples placed inside the membrane and outside of the vessel (underneath the heating tape), were used to monitor the temperatures and determine the temperature gradient within V2. Pressure transducers (Omega Engineering Limited, UK) were connected to both vessels to monitor the pressures. All tubing and parts were Sulfinert®-treated wherever possible to prevent adsorption of impurities to surfaces.

Before commencing the enrichment experiment evacuation of the vessels were performed using a combination of scroll vacuum pump followed by turbomolecular pump with penning gauge (Oerlikon Leybold, UK) and residual gas analyser (Kurt J. Lesker, UK) to monitor pressure and the moisture and air within the vessel. The vessels were evacuated down to  $1 \times 10^{-6}$  mbar and then pressurised with the gas mixture, this was repeated at least three times before starting the enrichment process to fully purge the system.

##### 3.1.2 Gas analysis techniques

The enrichment device can be used in conjunction with any analytical method that can be used to perform hydrogen purity analysis. ISO 14687-2:2012 lists several instruments that could be used which includes gas chromatography with various detectors, cavity ringdown spectrometry and Fourier-transform infrared spectroscopy.<sup>3</sup> For the studies performed in this paper an Agilent 7890A GC-PDHID (Agilent, UK) was used to perform

accurate measurements of nitrogen, methane, carbon monoxide and krypton in hydrogen at the range of 1-200  $\mu\text{mol mol}^{-1}$ . The GC contained HayeSep A, Molsieve 5A PLOT and Rt®-Q-Bond columns (Restek, UK). A single method was developed to measure all four components in one run and a heart-cutting technique was applied to split and divert the majority of the hydrogen matrix away from the detector to improve resolution in order to effectively measure the other analytes.<sup>9</sup> A typical chromatogram for a mixture containing  $\sim 2 \mu\text{mol mol}^{-1}$  of oxygen, nitrogen, methane and carbon monoxide in hydrogen is shown in Figure 4.



**Fig. 4** Example GC-PDHID chromatogram from the measurement of a calibration gas standard containing  $\sim 2 \mu\text{mol mol}^{-1}$  of oxygen, nitrogen, methane and carbon monoxide in hydrogen

Alternate injection of the standard and enriched gas mixture was performed to incorporate any effects of detector drift and the standard uncertainties were determined using the

##### 3.1.3 Hydrogen gas mixtures and calibration gas standards

Gas standards of hydrogen were prepared gravimetrically in 10 litre cylinders (BOC, UK) in accordance with ISO 6142:2001<sup>10</sup> from pure hydrogen (Air Products), nitrogen (Air Products, UK), carbon monoxide (Scott Speciality Gases, UK), methane (CK Gases, UK) and krypton (BOC, UK). Any impurities that were detected in these pure gases were quantified and these values were then incorporated into the final determination of the gas mixture compositions and uncertainties. For the purpose of this paper the gas standards that were used to perform the enrichment experiments will be referred to as gas mixtures, and the gas standards that were used to calibrate the analytical instruments will be referred to as calibration gas standards. Before use, the gas mixtures were verified against traceable primary reference gas standards. A list of the gas mixtures used is shown in Table 2.

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**Table 2** Hydrogen gas mixtures used in the enrichment tests

| Component                                  | Mixture A       |                                      | Mixture B       |                                      |
|--|-----------------|--------------------------------------|-----------------|--------------------------------------|
|  | Amount fraction | Gravimetric uncertainty <sup>a</sup> | Amount fraction | Gravimetric uncertainty <sup>a</sup> |
| Carbon monoxide / $\mu\text{mol mol}^{-1}$ | 1.8962          | 0.0074                               | 1.4225          | 0.0044                               |
| Krypton / $\mu\text{mol mol}^{-1}$         | 1.8747          | 0.0054                               | 1.4064          | 0.0022                               |
| Methane / $\mu\text{mol mol}^{-1}$         | 2.0077          | 0.0080                               | 1.5063          | 0.0048                               |
| Nitrogen / $\mu\text{mol mol}^{-1}$        | 2.0234          | 0.0734                               | 1.5371          | 0.0880                               |

<sup>a</sup> Expanded uncertainties based on standard uncertainties multiplied by a coverage factor  $k = 2$ , providing a coverage probability of approximately 95 %.

### 3.2 Enrichment methods

#### 3.2.1 Non-ideal gas law enrichment method

The hydrogen impurity enrichment device was set up as shown in Figure 2 and leak tested. The cylinder containing the gas mixture to be enriched was connected to the device inlet and the entire system including sampling inlet was evacuated through NV6 down to  $1 \times 10^{-6}$  mbar (with NV1, NV2 and NV3 open). NV3 was then closed and the vessels were left to reach room temperature. The gas cylinder containing the hydrogen mixture was opened to allow V2 to reach 10 bar (upon heating the vessel the pressure would reach 20 bar) after which NV2 was closed to allow V1 to fill to approximately 100 bar.

Once the vessels were filled, NV1 was closed and the system was again left to reach room temperature. The pressures and temperatures of the vessels were checked to ensure that the system had reached equilibrium and then these values were recorded. The heater for V2 was activated to allow the membrane to reach 300 °C. This allowed hydrogen from V2 to pass through the membrane and by opening NV4 the outlet flowrate was measured, this was usually above  $100 \text{ ml min}^{-1}$  at standard temperature and pressure (STP). Once the pressure in V2 had dropped close to 5 bar, NV2 was temporarily opened to allow the pressure to increase to 20 bar. This was repeated until the pressures in both vessels had reached a suitable pressure (~9 bar) for providing a high enrichment factor whilst leaving enough gas for performing analysis. NV2 and NV4 were then closed and the heater was turned off. The final pressure and temperatures were recorded once the system had cooled down to room temperature and reached equilibrium. This process typically required 4-5 hours but further optimisation of the system could be performed, for example by selecting a membrane with higher permeation rates, which would reduce this time.

To calculate the CEF, the recorded measurements of the pressure and temperature (along with volumes and compressibility factors) were substituted into equation (4) and the composition of the enriched gas mixture (V2) was measured by

flowing gas from NV5 (with NV6 closed and NV3 open) directly into the GC-PDHID.

#### 3.2.2 Tracer enrichment method

The tracer enrichment method used the same system and procedure as the non-ideal gas law enrichment method (as described in Section 3.2.1).

For the purpose of validating the tracer enrichment method, the amount fractions of krypton in the hydrogen mixtures are known from their gravimetric preparation, whereas in practice the krypton would be added to the hydrogen sample obtained by the laboratory. The krypton amount fraction (before enrichment) would then be measured using the analyser. A contribution has been included into the uncertainty budget to account for this (Section 4.2).

## 4. Results and discussion

### 4.1 Tracer enrichment method validation

Validation of the tracer enrichment method was performed using gravimetrically prepared gas mixtures containing nominally 1.5 - 2  $\mu\text{mol mol}^{-1}$  of carbon monoxide, methane and nitrogen. The gravimetric amount fractions and uncertainties of the two mixtures used are listed in Table 2. In addition to measuring the krypton amount fraction after enrichment, the pressures and temperatures of both vessels before and after enrichment were recorded in order to also enable the non-ideal gas law enrichment method to also be used. These measurements were additionally used as a simple way of monitoring the CEF during the experiment to ensure an enrichment factor of approximately 60 had been obtained. The CEFs calculated from both enrichment methods are shown in Table 3. Table 4 shows the gravimetric amount fractions of the impurities in mixtures A and B and the calculated amount fractions using both of the enrichment methods.



**Table 3** CEFs calculated by the non-ideal gas law and tracer enrichment methods

| Measurement  | Mixture A         |                     | Mixture B         |                    |
|--|-------------------|---------------------|-------------------|--------------------|
|  | Before enrichment | After enrichment    | Before enrichment | After enrichment   |
| V1 Pressure / bar                                  | 79.55             | 10.57               | 92.48             | 11.38              |
| V1 Temperature / °C                                | 21.2              | 19.0                | 17.5              | 18.9               |
| V1 Volume / cm <sup>3</sup>                        | 1065              | 1065                | 1065              | 1065               |
| V2 Pressure / bar                                  | 10.50             | 3.91                | 21.63             | 4.31               |
| V2 Temperature / °C                                | 21.2              | 19.0                | 17.5              | 18.9               |
| V2 Volume / cm <sup>3</sup>                        | 310               | 310                 | 310               | 310                |
| <b>CEF (non-ideal gas law)</b>                     | <b>58.69</b>      |                     | <b>65.73</b>      |                    |
| Krypton amount fraction / $\mu\text{mol mol}^{-1}$ | 1.87 <sup>a</sup> | 106.72 <sup>b</sup> | 1.41 <sup>a</sup> | 56.04 <sup>b</sup> |
| <b>CEF (tracer)</b>                                | <b>56.92</b>      |                     | <b>39.84</b>      |                    |

<sup>a</sup> Krypton amount fraction calculated gravimetrically <sup>b</sup> Krypton amount fraction calculated from analysis

**Table 4** Calculated amount fractions of impurities in Mixture A and B using the non-ideal gas law and tracer enrichment methods

|  | Calculated amount fraction of Mixture A |                                     |                          | Calculated amount fraction of Mixture B |                                     |                          |
|--|---|-------------------------------------|--------------------------|---|-------------------------------------|--------------------------|
|  | Gravimetric amount fraction             | Non-ideal gas law enrichment method | Tracer enrichment method | Gravimetric amount fraction             | Non-ideal gas law enrichment method | Tracer enrichment method |
| Carbon Monoxide / $\mu\text{mol mol}^{-1}$ | 1.896                                   | 1.697 (-10.5 %)                     | 1.749 (-7.8 %)           | 1.423                                   | 0.949 (-33.3 %)                     | 1.565 (+10.0 %)          |
| Methane / $\mu\text{mol mol}^{-1}$         | 2.008                                   | 2.027 (+1.0 %)                      | 2.090 (+3.1 %)           | 1.506                                   | 0.972 (-35.5 %)                     | 1.603 (+6.4 %)           |
| Nitrogen / $\mu\text{mol mol}^{-1}$        | 2.023                                   | 2.123 (+4.9 %)                      | 2.189 (+8.2 %)           | 1.537                                   | 1.576 (+2.5 %)                      | 2.599 (+69.1 %)          |

<sup>a</sup> Values in brackets represent the percentage difference from the gravimetric amount fractions.

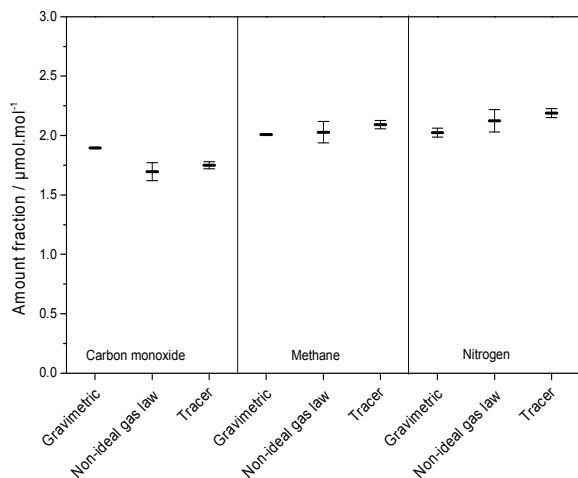
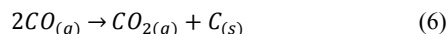
**Fig. 5** Calculated amount fractions of carbon monoxide, methane and nitrogen in Mixture A using the non-ideal gas law and tracer enrichment methods

Figure 5 shows the calculated amount fractions from the enrichment test using mixture A. This indicates that both of the enrichment methods obtained results that were close to the gravimetric amount fractions for all three impurities with a maximum variance of  $0.199 \mu\text{mol mol}^{-1}$  (a relative difference of 10.5 %) for the non-ideal gas law enrichment method when

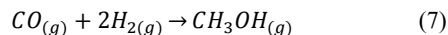
measuring carbon monoxide. In comparison to the non-ideal gas law enrichment method, the tracer enrichment method gave results with slightly lower variance from the gravimetric amount fractions (a maximum difference of 8.2 % for the measurement of nitrogen). However, comparatively there appears to be little difference to the results obtained using both methods. One important point to note is that the measurements obtained for the non-ideal gas law enrichment method have a much larger uncertainty compared to the tracer enrichment method (this will be discussed in more detail in Section 4.2). Because of this, the measurements for methane and nitrogen using the non-ideal gas law agreed with the gravimetric amount fractions within the assigned uncertainty. In the case of carbon monoxide, it is apparent that neither enrichment method produced results that agreed with the gravimetric amount fraction within the uncertainty of the measurement.

The reasons for this may not be entirely due to errors in the CEF calculation. An increase in nitrogen amount fraction was observed during the experiments performed by Papadias *et al.* and although it was not explained in the paper this could have been caused by an air leak. This may not be unexpected considering that the high temperatures applied to V2 could have caused expansion and contraction of the connecting pipework and connections. However, this factor alone is not likely to explain the lower amount fraction calculated for carbon monoxide (also experienced by Papadias *et al.*). The reason for this could be due

to carbon monoxide adsorption onto the palladium membrane.<sup>11</sup> Another explanation could be that reactions had occurred between the impurities, this is entirely possible considering that the impurities are subjected to temperatures as high as 300 °C in the presence of catalytic metals. The Boudouard reaction<sup>12</sup> is viable at temperatures below 700°C, which could explain the under-measurement in carbon monoxide:

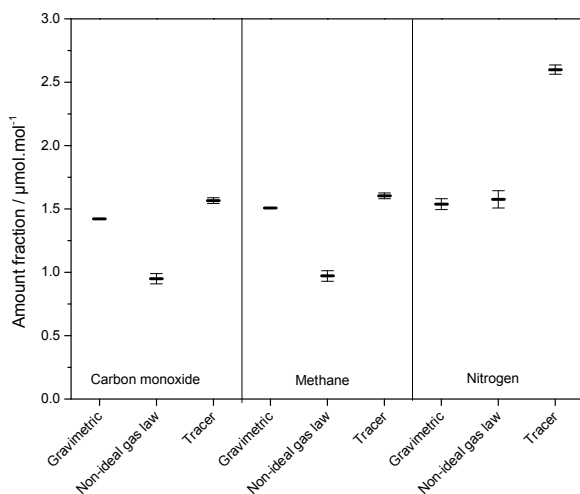


Another possible explanation is the production of other components, for example methanol, which could occur *via* the following reaction<sup>13</sup>:



Papadias *et al.* also listed several other reactions that were possible which would change the composition of the impurities in the gas mixture resulting in a loss of carbon monoxide.<sup>6</sup> Although it was noted that these reactions may have occurred, this was not confirmed during the tests because the analytical method used did not measure the products of these proposed reactions such as carbon dioxide, water or methanol.

Whereas the tracer enrichment test with mixture A gave a carbon monoxide amount fraction lower than the gravimetric value, during the test using mixture B (see Figure 6), the measurement of carbon monoxide using the tracer enrichment method was shown to be slightly higher than the gravimetric amount fraction.



**Fig. 6** Calculated amount fractions of carbon monoxide, methane and nitrogen in Mixture B using the non-ideal gas law and tracer enrichment methods

As the amount fraction of carbon monoxide in mixture B is lower than in mixture A, it is possible that carbon monoxide may have adsorbed onto the vessel or membrane during the enrichment test using mixture A and subsequently desorbed in the presence of mixture B. Alternatively there could have been an additional component of uncertainty that was not considered and incorporated into the uncertainty calculation.

## 4.2 Uncertainties

Even if the hydrogen impurity enrichment device does succeed at correctly determining an impurity amount fraction, the result alone is meaningless unless it is associated with a determination of the uncertainty. Ideally the uncertainty will be suitably low but in the case of impurity enrichment even a measured value with a relatively large uncertainty is favoured over using an analyser that is not able to detect the impurity at all (a value associated with the limit-of-detection would be provided instead). The uncertainties for both of the enrichment methods discussed in Section 2.1 can be calculated from the uncertainties in each of the parameters that form the CEF measurement equation by use of an uncertainty budget. Full details regarding determination of measurement uncertainty are given in the Guide to Uncertainty in Measurement.<sup>14</sup>

Uncertainty budgets have been developed to calculate the overall expanded uncertainty for both methods based on a 60-fold enrichment of  $2 \mu\text{mol mol}^{-1}$  of nitrogen, methane, carbon monoxide and krypton in hydrogen at 120 bar. The data used for the uncertainty budget were those obtained from the enrichment test performed in Section 4.1 using mixture A. The results of the uncertainty budget are shown in Table 5, and Figures 7 and 8a show the main contributors to the uncertainty for both enrichment methods. Figure 8b shows a summary of the individual uncertainties that were combined to calculate the overall uncertainty for  $n_{2,a}$  in Figure 8a.

For the tracer enrichment method the CEF is calculated using equation (5). As the purpose of the enrichment tests was to validate the tracer enrichment method, the krypton amount fraction in the gas mixture ( $y_{Kr,a}$ ) was determined gravimetrically instead of by analysis (which would be done in practice), therefore a 0.5 % relative uncertainty was assigned to  $y_{Kr,a}$  as a reasonable estimation for GC-PDHID repeatability. A relative uncertainty of 0.2 % was assigned to  $b$  to account for non-linearity of the GC-PDHID system. As Figure 7 shows, the main contributors to the uncertainty are  $A_{Kr,b}$ ,  $A_{Kr,st}$  and  $y_{Kr,a}$  and this is due to the repeatability of the GC-PDHID. The uncertainty of  $y_{Kr,st}$  is low as this is associated with the gravimetric uncertainty of the krypton amount fraction in the calibration gas standard.

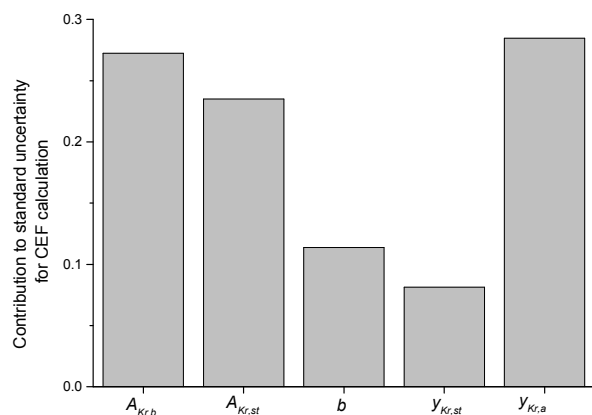
The uncertainty contributions for the non-ideal gas law enrichment method shown in Figure 8b were generally determined using information provided by the suppliers of the equipment used to construct the enrichment device. For measurement of the pressure and temperature, the main uncertainties were a result of instrument calibration and resolution. For the thermocouples an uncertainty in temperature of  $\pm 5$  K was assigned to account for temperature gradients within the sampling vessel. For the volume measurements of V1 and V2 (where a large uncertainty of  $10 \text{ cm}^3$  was provided by the supplier) the uncertainties were determined by filling the evacuated vessels with 100 bar of pure nitrogen gas and measuring the change in mass. The volume could then be determined using the non-ideal gas law as shown by equation (1). Compressibility was calculated using the Soave-Redlick-Kwong equation<sup>15</sup> and the obtained compressibility factors were validated against chemical reference data.<sup>16,17</sup> The overall uncertainty for the compressibility factor was high because the

Soave-Redlick-Kwong equation involved components of the pressure and temperature, both of which possessed a significant uncertainty.

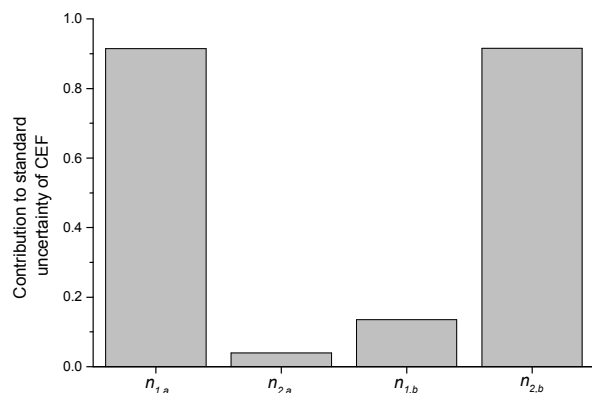
**Table 5** CEFs and uncertainties determined for the enrichment tests performed with mixture A

| Enrichment method | CEF   | Uncertainty <sup>a</sup> |
|-------------------|-------|--------------------------|
| Non-ideal gas law | 58.69 | 2.6                      |
| Tracer            | 56.92 | 1.0                      |

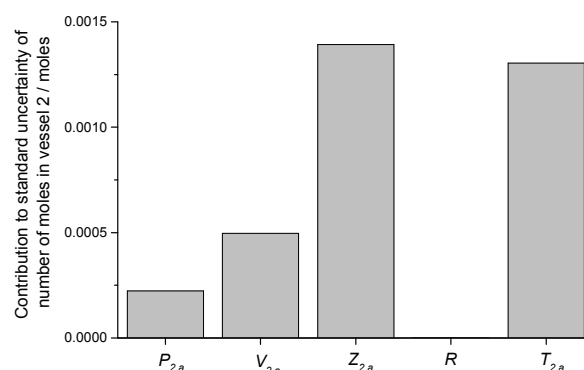
<sup>a</sup> Expanded uncertainties based on standard uncertainties multiplied by a coverage factor  $k=2$  (providing a coverage probability of approximately 95%).



**Fig. 7** Contributing factors to the overall uncertainty for the tracer enrichment method (represented by equation (5))



**Fig. 8a** Contributing factors to the overall uncertainty for the non-ideal gas law enrichment method (represented by equation (3))



**Fig. 8b** Contributing factors to the overall uncertainty for calculation of  $n_{2,a}$  in Figure 8a

Although both enrichment methods have performed successful measurements, the uncertainty budgets presented in this section indicate that the tracer enrichment method performs a more accurate analysis by providing a ~60 % lower relative uncertainty for CEF compared to the non-ideal gas law enrichment method.

### 4.3 Air leak and membrane failure

Figure 5 shows that both enrichment methods performed sufficiently well to quantify the three impurities in mixture A. The results from using mixture B (Figure 6), however, indicated that this test had not occurred as expected, with an amount fraction much lower than the gravimetric value being measured for carbon monoxide and methane using the non-ideal gas law enrichment method. A higher amount fraction for nitrogen than the gravimetric value was measured using the tracer enrichment method. A reason for these results could be that an air leak had occurred during enrichment - this was confirmed by observing a response on the GC-PDHID chromatogram corresponding to an amount fraction of oxygen at around  $5 \mu\text{mol mol}^{-1}$  in the enriched gas mixture.

A high pressure leak test was performed at room temperature before using the enrichment device and this indicated that all of the connections were sufficiently leak free, however when V2 was subjected to a higher temperature it is possible for a small air leak to have occurred at one of the connections. This could have allowed some of the hydrogen (including impurities) to escape and air to enter the system, which in turn would increase the amount fraction of nitrogen in the gas mixture (as confirmed by the tracer enrichment method calculation). For the non-ideal gas law enrichment method this would reduce the actual enrichment factor (hence the under-estimation of the amount fractions of carbon monoxide and methane). A molar balance of the enrichment system was performed by calculating amount of gas lost during enrichment (obtained from the non-ideal gas law enrichment method results) and the amount of air added to the system (obtained from the tracer enrichment method results). The molar balance indicated that  $9.2 \times 10^{-3}$  moles of hydrogen were lost through a leak and  $2.1 \times 10^{-6}$  moles of air entered the system during enrichment, thus confirming the air leak.

Even though the results indicate that an air leak had occurred, it is evident that the measurements of carbon monoxide and methane by the tracer enrichment method were still accurate,

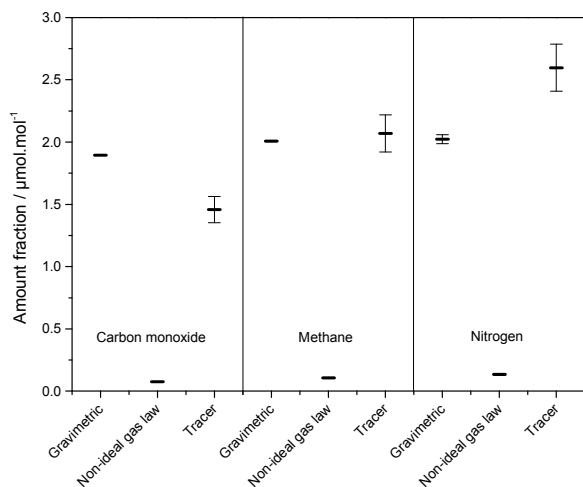
which is explained by the co-variance phenomenon as detailed in Section 2.1.2: the loss of hydrogen through the leak would also allow a small loss of impurities, but it would be expected that the ratio of carbon monoxide and methane to krypton would remain the same. As the tracer enrichment method calculates the CEF by measuring the difference in krypton amount fraction before and after enrichment, this value is still valid for determining the amount fractions of carbon monoxide and methane. However, this would not apply for measurement of nitrogen (or oxygen) as the addition of air from the atmosphere into the system would not be accounted for during calculation of the tracer enrichment method CEF. For the non-ideal gas law enrichment method, the loss of gas mixture through the leak would result in an erroneously high CEF for all components (except for nitrogen and oxygen if measured). This is because it would assume that the gas that was lost by the leak was actually permeation of hydrogen out of the vessel through the palladium membrane. The results also indicate that during an air leak the measurement obtained for nitrogen as calculated by the non-ideal gas law enrichment method agreed well with the gravimetric value. However, the molar balance indicates that the change in CEF during an air leak was predominantly influenced by the loss of hydrogen rather than the influx of air, so the matching result is most probably a co-incidence.

The results therefore show that a major difference between the two enrichment methods is that whereas the non-ideal gas law enrichment method may not be able to accurately quantify measurements of impurities during an air leak, the tracer enrichment method would be able to do so due to the co-variance phenomenon. However, during an air leak use of the tracer enrichment method alone would not allow accurate quantification of nitrogen and air (because the leak would not be detected), so the ideal solution would be to perform enrichment using both methods, where quantification of the impurities are performed using the tracer enrichment method and the non-ideal gas law enrichment method is used to identify any possible air leak and monitor the CEF during enrichment. If an air leak did occur, the tracer enrichment method could still be used to measure the amount fraction of all of the impurities apart from nitrogen and oxygen.

This approach would also work well in the case of a membrane failure, which is shown by the results in Figure 9 where a second experiment was performed using mixture A. During this experiment, the pressure in the vessels dropped at a similar rate as in the previous experiments, but as Figure 9 shows the results from the non-ideal gas law enrichment method were very different to both the tracer enrichment method results and the gravimetric amount fractions of the impurities in the gas mixture.

According to the tracer enrichment method the CEF was less than 3 even though the non-ideal gas law enrichment method gave a CEF of around 57. This is evidence that a major leak had occurred, and is more likely to have been a leak through the membrane rather than at the vessel connections as a molar balance suggests that the influx of air into the system was negligible ( $2.33 \times 10^{-6}$  moles) compared to the amount of gas mixture lost (0.0915 moles). As the enrichment factor was very low the amount fractions measured after enrichment were also low (therefore the signals were noisier) leading to larger uncertainties for the tracer enrichment method during analysis compared to the previous tests (as shown by the large error bars for the tracer enrichment method results in Figure 9).

Following this test, the palladium membrane was removed from V2 and was found to have deformed. Figure 10(a) shows an image of the membrane before use where it was straight with a very smooth surface. Following the second enrichment test using mixture A, the membrane had changed shape and the surface had become corrugated (Figure 10(b)). Although part of the membrane was damaged during the removal of the membrane from V2 (as the membrane had become fragile and coiled so would no longer slide out easily), there was no clear evidence of membrane cracking which would only be expected to be observed using advanced optical techniques such as scanning electron microscopy. However, as Figure 10(b) shows it is clear that the membrane had experienced buckling collapse.



**Fig. 9** Calculated amount fractions of carbon monoxide, methane and nitrogen from the second experiment with mixture A using the non-ideal gas law and tracer enrichment methods



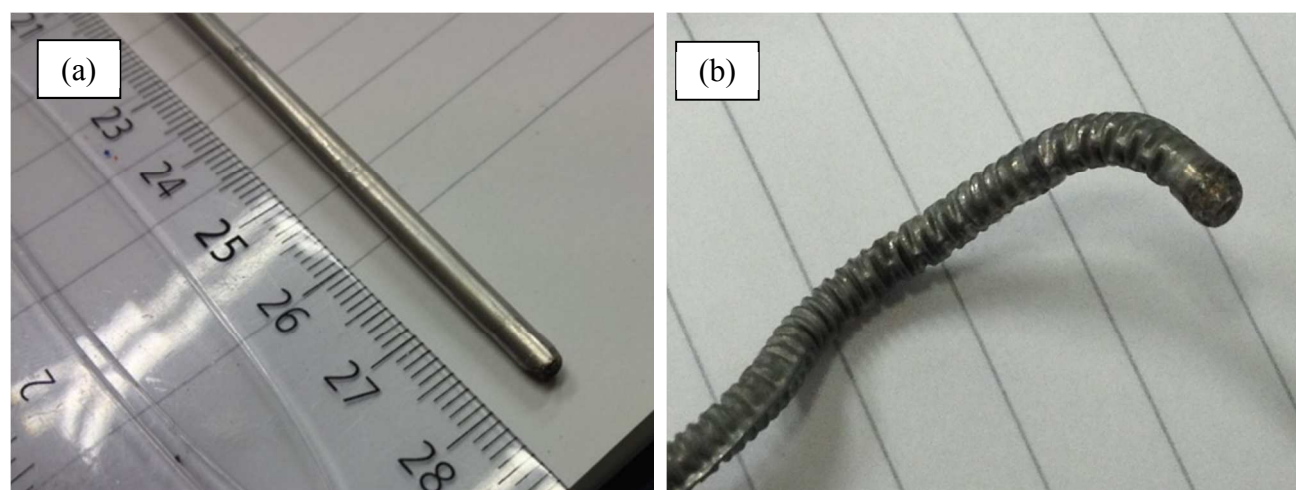


Fig. 10 Membrane used in enrichment device (a) before use and (b) following suspected membrane failure

Membranes such as the one used in this enrichment device are not usually required to be replaced on a frequent basis and theoretically would only be damaged if the conditions applied to the membranes were not in compliance with their operating specifications. However, even when using the standard operating conditions there is no guarantee that the membrane would not fail. Membrane failure could occur if the user accidentally exceeds the maximum pressure, another part of the device becomes faulty or if the membrane itself was damaged before placing into the device. If the tracer enrichment method is not used in parallel with the non-ideal gas law enrichment method, there would be no way of identifying when there is membrane failure. This confirms the importance of using both enrichment methods simultaneously as this allows the membrane to be replaced as soon as failure is detected and before erroneous results are produced.

#### 4.4 Enhancing enrichment

The novel tracer enrichment method presented in this paper has significantly advanced existing hydrogen enrichment techniques, but there are additional modifications that could lead to further improvement. As an example, the enrichment factors achieved in this paper did not exceed 60. The enrichment factor is limited by the amount of the gas mixture that is contained in the device, which is dictated by the starting pressures of the gas mixture and the volumes of the vessels. As an example, the pressure of the gas in V1 could theoretically be increased to maximise enrichment as long as the safe working pressure of the vessels is not exceeded. Another solution would be to reduce the volume and final pressure (following enrichment) of V2 but this could lead to problems during measurement of the enriched impurities as there would be a very small amount of gas mixture left to perform analysis of the enriched gas mixture. One viable solution may be to increase the volume of V1. For example, replacing V1 with a 10 litre gas cylinder (containing the hydrogen sample at the same initial pressure) would lead to a ~9-fold increase in enrichment. Indeed even a 50 L gas cylinder could be used instead which would allow a theoretical enrichment factor of above 2000. The feasibility of using higher volumes or pressures

would be dependent on whether it would be possible to attain such samples from a hydrogen refueller every time a purity analysis is required. Bossard *et al.* installed the hydrogen enrichment chamber within a mass spectrometer, which allowed measurement of the impurities within the chamber at very low pressures (less than  $1 \times 10^{-7}$  mbar). Enabling the vessel pressure to drop this low during enrichment is a very effective way of increasing the enrichment factor. Using this set-up, high enrichment factors could be achieved using small samples of hydrogen that can be easily taken from hydrogen refuellers (e.g. 15 bar sample in a 1 L vessel).

Another aspect of the hydrogen enrichment device worthy of further investigation is the behaviour of the impurities during enrichment, which may include adsorption of components (e.g. sulphur compounds) onto the vessel or membrane and side-reactions that may occur between the impurities. These effects may ultimately be avoided by selection of an appropriate membrane. For the tests performed in this paper a palladium-silver alloy coated with palladium-copper membrane was used but it could be possible to utilise other types of membranes which may prevent adsorption of components such as sulphur compounds or speed up the enrichment process by providing faster permeation rates. It may also be possible to avoid using membranes entirely by utilising alternative separation techniques such as pressure swing adsorption.<sup>18</sup>

The work in this paper has focused on performing enrichment of impurities in hydrogen, but the same method could be applied to other gases simply by selecting a different membrane. As an example, perovskite membranes such as  $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$  or  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CO}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  can be used to selectively remove oxygen out of a sample, thereby enriching the remaining impurities.<sup>19</sup>

## 5. Conclusions

A novel tracer enrichment method for enriching the impurities in hydrogen has been presented and validated. The method, which calculates the enrichment factor by measuring the change in concentration of an added tracer component (krypton), was compared against the non-ideal gas law enrichment method proposed by Papadias *et al.* where the enrichment factor was



calculated by monitoring changes in pressure and temperature.<sup>6</sup> Both enrichment methods were validated by determining the composition of a hydrogen mixture containing  $\sim 2 \mu\text{mol mol}^{-1}$  of nitrogen, methane and carbon monoxide after applying an enrichment factor of  $\sim 60$ . The results indicated that both enrichment methods were able to determine calculated enrichment factors that generally agreed with those calculated from analysis of the enriched mixture. Uncertainty budgets were developed which indicated that the results from the tracer method had  $\sim 60\%$  less relative uncertainty than the non-ideal gas law enrichment method. Another advantage of the tracer enrichment method was that it could still accurately determine the amount fraction of all impurities (other than nitrogen and oxygen) during an air leak or membrane failure; this currently cannot be achieved using the non-ideal gas law enrichment method.

It was also concluded that a combination of both enrichment methods would constitute the ideal method for performing accurate measurements of trace level impurities in hydrogen whilst being able to monitor the enrichment factor and identifying problems such as membrane failure or air leaks. Further investigations however need to be performed to assess the effects of adsorption or reactions of impurities and also to make improvements to the system so that it can be easily used to perform enrichment measurements from a small volume sample taken from a hydrogen refueller.

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