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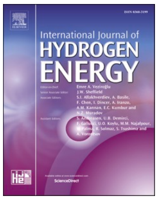

Advancing hydrogen leak detection: Design and calibration of reference leaks

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A B S T R A C T

The introduction of hydrogen into the gas grid requires stricter safety measures due to its enhanced flammability compared to natural gas. Detecting small hydrogen leaks is crucial for meeting health and safety requirements, given hydrogen's potential for easy ignition and the hazards associated with its combustion. This paper presents an overview of the quantification of small hydrogen leaks, regarding conversions between common units of measurement, namely concentration and leak rate. In addition, the need for traceable assessments of hydrogen leakage was also considered, which included proposal of the design, calibration, and metrological evaluation of portable hydrogen reference leaks in the range of 10^{-6} to 10^{-4} Std cm^3/s, the latter being considered as the lowest side of the range of interest for quantifying hydrogen leaks. Two methods of manufacturing leak artefacts, namely conductance and permeation, are explored, and the produced leaks were used to test two hydrogen leak detectors with different working principles. A calibration technique based on a constant pressure gas flowmeter is described together with the uncertainty budget. The study provides insights into the challenges of calibrating detectors for hydrogen leaks, highlighting the importance of traceability in ensuring safety and environmental protection in the context of hydrogen infrastructure. It was demonstrated that reference leaks are highly suitable to test hydrogen leak detectors in the mentioned flow range due to their simplicity, high reliability, low depletion rate and high portability.

1. Introduction

The introduction of hydrogen in the gas grid, as part of the European policy of transition to cleaner sources of energy [1], while also reducing the dependence in fossil fuels and potentially improve urban air quality [2], brings extra safety requirements when compared to what currently stands for natural gas [3]. Hydrogen is seen as a solution to achieve carbon neutrality worldwide, being recognised as an ideal energy carrier and clean energy provider [4]. As hydrogen has stronger flammable properties than natural gas, due to the larger flammability domain and lower ignition energy for instance, stricter tightness requirements are expected for the hydrogen gas and hydrogen-enriched natural gas network, from production to storage and distribution [2,5–8]. The definition of maximum allowable leaks is paramount to select which leak detectors should be used in leak detection campaigns and to prepare the metrology chain to establish the traceability in SI units of all measuring instruments [9].

There are several drivers for emission monitoring. Only massive hydrogen leaks have economical relevance and those can be detected in real time by pressure drop or multiple flow measurements in pipelines. The relative ease with which hydrogen can ignite, with an often-invisible flame and its eagerness to burn or form explosive mixtures with air, especially in confined spaces, has been the main historical driver to detect hydrogen leaks [7]. However, the relatively recent discovery that hydrogen, through its impact in the lifetime of methane on the atmosphere, has a not negligible global warming potential, has led to increasing drivers to detect and report methane emissions for environmental purposes [10,11]. This leads to the need to implement a similar framework of environmental controls such as leak detection and repair (LDAR) programmes and emission reporting.

The pertinent techniques to effectively detect small leaks in the gas grid involve the use of quantitative and gas-selective detectors [12], though other, more complex techniques, relying on different physical principles, such as Particle Image Velocimetry (PIV) and some others,

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have been studied by some researchers, as mentioned in Ref. [13]. The presence of hydrogen near the gas lines exceeding its concentration in the atmosphere will signal the existence of leaks. Since small leaks are normally precursors to larger ones, their detection allows for proper monitoring and maintenance of the hydrogen grid, thereby improving safety. However, it is worth noting that, as stated in Ref. [5], hydrogen has a diffusion coefficient into air about 4 times greater than methane's. This means that, when a probe is placed at a certain distance from a leak source, the reading for a hydrogen leak is lower than for the same leak with methane, as hydrogen is more diluted in the surrounding atmosphere probed by the sensor. Therefore, while existing regulations and guidelines for Volatile Organic Compounds (VOC's) can and should be used as starting points for detection of hydrogen, such as the EN 15446, they must be adjusted accordingly considering its different properties.

There is a wide variety of concentration-based leak detectors, measuring different quantities and covering very different ranges. The most common leak detectors measure the concentration of the target gas. Some can detect low ppm concentrations (vol/vol), while others work in the percentage range (≈0.1–100%). Some are portable, while others are stationary and only suitable as room monitors.

In leak detection, besides locating leaks, it is relevant – and perhaps more important – to know how large they are. This is especially true in industrial scenarios, where a certain degree of leakage is almost inevitable. Yet, these leaks might not reach a scale that poses safety risks, environmental harm, or economic viability for repair. This reinforces the need to establish values for the maximum admissible leaks for hydrogen in various conditions, similarly to what currently happens with the natural gas infrastructure [9].

Portable detectors are the instruments of choice for locating leaks. However, their reading depends on the position of the probe relative to the leak source, the angle between the probe and the flow direction, and the leak geometry. Hence having standardised sampling procedures is very important. A special reference should be given to instruments such as the Bacharach Hi Flow Sampler which are specially designed to quantify gas leaks from industrial sources [14].

Some leak detectors have a small pump to suck the gas into the sensor measuring the gas leakage diluted in air. These detectors can measure the actual leak rate only if the probe is close enough to the leak source ensuring that the entire leakage is sucked into the sensor. There is a second class of instruments able to suck high volumes, intended to draw in large leaks, plus background air. Based on the pumping speed, both classes of detectors can provide the leak rate and concentration. Since the first class of instruments produce a lower dilution rate, they are more sensitive, allowing the detection of 'small' leaks, which can be defined as those with a leak rate much lower than the probe pumping speed.

The relationship between the concentration c_{H2} and leak rate Q_{H2} is given by:

$$c_{H2} = \frac{Q_{H2}}{p \times S} \qquad \text{Eq.1}$$

where p is the total pressure (≈1 atm) and S is the pumping speed of the probe. Very often $S = 1\ \mathrm{cm^3/s}$ which means that if Q_{H2} is measured in atm.cm^3/s (or Std cm^3/s) then Q_{H2} and c_{H2} has the same numeric value. For example, a leak of 10^{-4} Std cm^3/s corresponds to a concentration of 100 ppm (or 10^{-4}). $S = 1\ \mathrm{cm^3/s}$ is common in mass spectrometry leak detectors. The concentration of hydrogen in the atmosphere is about 0.6 ppm. Therefore, this quantity can be viewed as the lowest useful concentration that leak detectors should measure. Even with background subtraction techniques, it is difficult to accept that concentrations below this limit can have any meaning in leak testing. In Table 1 conversion factors for some common leak rate units are presented.

Table 1
Conversion of leak rate units commonly used in leak detection.

Std[a] cm^3/s	Pa.m^3/s	ppm ($S = 1$ cm^3/s)	g/year (for H_2)
1	0,1013	1×10^6	2839

[a] Standard conditions $T = 273.15$ K and $p = 101325$ Pa.

The leak rate can also be ascertained from concentration measurements if the leakage point is properly covered with a hood or bag. If this bag has a known volume V, then the leak rate is given by:

$$Q_{H2} = \frac{c_{H2} V}{t} \qquad \text{Eq.2}$$

where t is the accumulation time.

The most straightforward method to ensure traceability to SI units in leak detection of 'small' leaks is by employing a calibrated reference leak [15]. When measuring a leak, its flow rate is compared to that of the reference leak. This method effectively overcomes issues commonly found in sensitive leak detectors such as drift, ageing, or uncalibrated detector, ensuring and confirming traceability of the flow rate. Consequently, these instruments only require in-situ testing against a reference leak, eliminating the need for laboratory calibration of the detectors themselves.

Reference leaks are small, portable artefacts designed to generate a known flow rate [16]. Typically including a gas reservoir, reference leaks in the range of 10^{-8} to 10^{-4} Std cm^3/s offer an almost constant flow for many years without the need of reservoir refilling, due to the very low depletion rate. Leaks above 10^{-4} Std cm^3/s need to be connected to a gas reservoir with the target gas at a well-defined pressure, since pre-filled reservoirs would deplete too quickly. For flow rates between 10^{-4} and 10^{-2} Std cm^3/s, reference leaks in the form of orifices or capillaries are commonly utilised. In cases of even higher flow rates, continuous calibrators equipped with a needle valve and a flowmeter prove to be more convenient. Most reference leaks are often produced with helium and can be calibrated in many accredited laboratories. Helium-based leak detection is a well-established and widely employed technique, particularly in applications demanding stringent levels of tightness. The traceability of leak detection using helium detectors is robust and widely acknowledged. However, reference leaks for hydrogen are still difficult to find worldwide and even more difficult is to find laboratories offering traceable calibrations for hydrogen flow rates in the required range.

This paper discusses suitable designs to produce portable hydrogen reference leaks in the range between 10^{-6} and 10^{-4} Std cm^3/s (equivalent to 1–100 ppm when applying Eq. (1) with a typical probe with $S = 1$ cm^3/s) which is expected to cover the smallest leak rate of interest for hydrogen related applications. Detailed design specifications are provided as well as the metrological evaluation of the produced artefacts. An adequate calibration technique is also described along with a typical uncertainty budget. With the introduction of hydrogen into the gas grid, a substantial increase in demand for these artefacts and their calibration is anticipated. The main aim of this contribution is to enable easily traceable assessments of hydrogen leakage, relying on high-quality reference leaks.

One must keep in mind that leak detection and quantification does not ensure 'zero' leakage, but rather a leakage smaller than the instrument's detection limit. Thus, the use of sensitive instruments which are able to quantify leak rates down to ≈10^{-5} Std cm^3/s (0.028 g/year) can only warrant that the leakage in a single potential source is lower than that limit. If a 'leak tight' transmission network has one million of similar potential sources the whole leakage can be as much as 28 kg/year. This emphasizes the need of quantification for 'small' leaks.

2. Design of hydrogen reference leaks

Hydrogen reference leaks in the range of 10^{-6} to 10^{-4} Std cm^3/s should meet specific requirements. Artefacts should be compact for easy portability and exhibit a stable leak rate in the short (hours) and medium term (days), with predictability over the long term (several months). A general diagram of a reference leak is depicted in Fig. 1. It consists of a pressurised reservoir, a valve, and a restriction. A pressure gauge is optional but recommended. Gas flows continuously from the reservoir to the outlet via the restriction.

Portability is determined by the size of the reservoir which should conveniently be below 1 L, very often close to 0.3 L. Leaks of this size weigh in the order of 1 kg, making them easily transportable with the leak detector. The reservoir, typically made in stainless steel, is pressurised with hydrogen via the filling valve. Very often the valve handle is removed to avoid improper opening. The use of a pressure gauge is convenient to enable identifying any accidental pressure drop. The heart of the reference leak is its restriction. It is at this point that the flow of gas is defined. There are two common approaches for the restriction: conductance and permeation. A comprehensive review on these approaches is presented in Refs. [16,17].

Conductance leaks have an open passage of gas, normally with high constrictivity. They can be made in the form of crimped capillaries, tiny orifices, cracks, and compressed powders among other techniques [17]. In many cases, adjustments are normally made by trial and error, often requiring a long time to achieve the desired flow rate. Fine tuning is then made with the filling pressure. Some manufacturers have other proprietary solutions, probably the result of many refined attempts.

In permeation leaks the restriction consists of a selected dense material working as a gas membrane. Many polymers display a suitable permeability for hydrogen, such as polytetrafluoroethylene (PTFE). In a timescale of minutes hydrogen permeates PTFE leading to a constant flow rate within a few hours. The main advantage of permeation leaks is that they never become clogged as may happen to conductance restrictions.

Restrictions for hydrogen were produced following the designs in Fig. 2, based on both approaches. A conductance restriction was made by compressing polyetheretherketone (PEEK) particles (produced with a file) inside a small tube, as shown in Fig. 2 a). A stainless tube was partially crimped to hold the particles against a bolt which works as a piston compressing the powder. PEEK showed some advantage over metallic powders since a fine and reversible tuning of the leak rate is possible by tightening the bolt, even enabling achievement of a completely clogged restriction. The bolt thread has enough clearance, so it offers high conductance for gas to flow until the true restriction, the compressed powder. The open end of the tube was connected to a helium mass spectrometer leak detector (Adixen ASM 140D) to measure the flow rate after each step of compression. The leak rate was adjusted in several trials until a reading in the 10^{-7} Std cm^3/s decade was reached with helium at atmospheric pressure. Then the restriction was inserted inside a reservoir and pressurised with helium, while the leak rate was measured as a function of the filling pressure. Knowing that gas flow in the target range is normally in the transitional regime, the flow for H_2 was expected to be about 2 times higher than that of helium. Based on this, the required H_2 pressure was estimated, and the helium was replaced by hydrogen at that pressure. Finally, the artefact was left to stabilise prior to calibration.

Restrictions based on permeation elements are much easier to design. For the lower end of the target flow rate the permeation area was defined by small holes in a brass cylinder as depicted in Fig. 2 b). These holes were covered by a PTFE tube ⌀ 4 mm internal diameter (6 mm outer diameter) commonly used in gas lines. This tube was inserted by force over the polished brass piece. The hydrogen pressure was applied from outside to the central hole which was connected to the outlet tube. To build another leak for the upper flow range, the permeation area was defined by the length of the tube as shown in Fig. 2 c). At one end a brass cap was inserted. The other tube end was inserted in a brass piece with a drilled hole connected to the gas outlet tube. All tests were firstly made with helium using the leak detector. The same PTFE tube can be employed to achieve a 100-fold increase in hydrogen flow rate just by varying the permeation area.

Upon manufacturing artefacts, it is not uncommon that leaks in the lower end display a non-continuous flow rate. If the gas accumulates somewhere across the restriction in partially closed tiny pockets, it may produce small bursts of flow. This was previously observed by the authors in some restrictions of both types. Therefore, it is crucial to ensure that reference leaks remain stable not only in the medium and long term but also in the short term.

The constancy of the leak rate in the long term is defined by the amount of gas inside the reservoir which is proportional to its pressure p and reservoir volume V. The flow rate Q over time t is given by:

$$Q = Q_o e^{\frac{-Q_0 t}{pV}} \qquad \text{Eq.3}$$

where Q_o is the leak rate at $t = 0$. For a leak of 1×10^{-5} Std cm^3/s, $V =$ 0.3 L and $p \approx 10$ bar its flow rate after one year is only 10% lower. This quantity is designated as the depletion rate of a reference leak and also describes the loss in the reservoir pressure. The small decrease in the flow rate is not a problem since its time dependence is fully predictable by Eq. (3) (as long as the leaks are kept at a constant temperature or its variations with time are fully known). Therefore, the actual flow rate of a reference leak can be calculated at any time after the last calibration when Q_o was measured. The depletion rate is not only a function of Q_o but also of V and p. Thus, even reference leaks close to 1×10^{-4} Std cm^3/s can be built with acceptable depletion rate if p is increased (<20%). Increasing V is also possible but comes at the cost of portability.

From the discussion above it becomes understandable why these reference leaks should be permanently left open. Closing the leak will accumulate gas in the restriction and in the dead volume between the restriction and the valve. A similar effect would take place if the valve were placed before the restriction. Opening such a valve would re-establish the flow but a transient time of many minutes or hours would be required to deliver a constant flow. Moreover, any correction based on Eq. (3) would be compromised since the flowing time was interrupted. This is the reason why most reference leaks have no valve at the outlet. When available, it should be used only for short times (seconds or few minutes). In the case of hydrogen, the continuous flow does not represent any safety risk since the delivered amount gas is so small that its quick dispersion avoids any relevant concentration increase of hydrogen. The total amount of gas inside the reservoir is so small that even if liberated quickly in a small room of a few cubic metres it will never reach the Lower Explosive Limit (LEL).

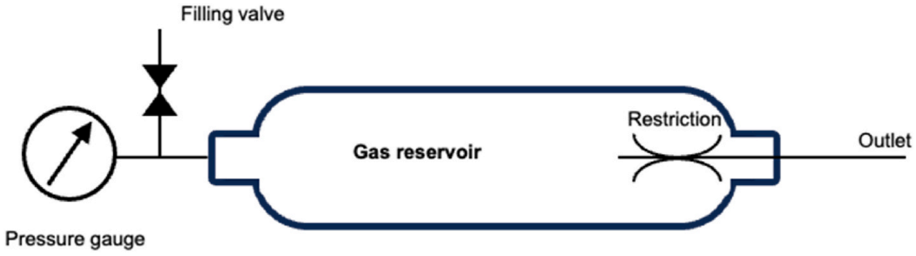

Fig. 1. Main elements of a reference leak with a gas reservoir.

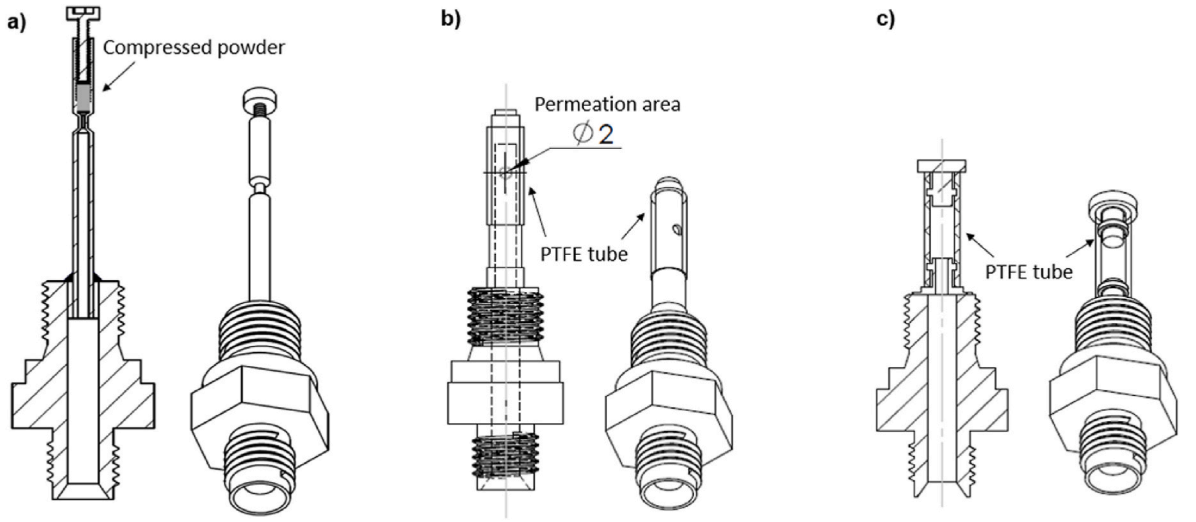

Fig. 2. Designs used to manufacture hydrogen reference leaks.

3. Calibration of reference leaks

3.1. Calibration method

Calibration methods for reference leaks are well described in ISO 20486 and well discussed in Ref. [16], and [18–20]. This standard describes seven different calibration methods covering the full range and the two typical delivery pressures - vacuum and atmosphere. Calibration against vacuum is usually performed for helium reference leaks due to its usual application in mass spectrometer leak detectors. Since hydrogen reference leaks are aimed to be used at atmospheric pressure, its calibration should be done at the same pressure. The G method from ISO 20486 is a suitable primary method, based on a constant pressure flowmeter. This method is suitable for working in the $[10^{-6}, 10^{-4}]$ Std cm^3/s range, as it will be shown. In the $\geq 10^{-4}$ Std cm^3/s range other methods are also suitable.

Most of the cited methods are independent of the gas type. However, hydrogen may more easily permeate through some materials, especially polymers commonly used in sealing. Moreover, in methods using the displacement of liquids, the solubility of small amounts of hydrogen should be evaluated.

In a constant pressure flowmeter, the reference leak is connected to a small and closed volume where the pressure is carefully monitored. A small piston, controlled by a stepper motor, is connected to the chamber. Whenever the pressure, p, is observed to rise, the piston expands the volume. The flow rate, Q, is determined by the ratio of the volume change, ΔV, by the elapsed time, Δt, as described in the following equation:

$$Q = \frac{d(pV)}{dt} = \frac{p\Delta V}{\Delta t} \tag{Eq.4}$$

The expansion is the result of discrete steps from the motor. Its extension should be carefully balanced with the flow rate of the reference leak, the chamber volume, and the gauge resolution to avoid major pressure variations. Ideally, every discrete expansion step should generate a pressure decrease close to the gauge resolution.

The previous equation assumes a constant temperature along the calibration time. Moreover, the constancy of the pressure cannot be guaranteed better than the gauge resolution. Therefore, to consider small variations in temperature and pressure Eq. (4) should be replaced by:

$$Q = \frac{p\Delta V}{\Delta t} + \frac{\Delta p\ V}{\Delta t} + \frac{p\ V\Delta T}{T\Delta t} \tag{Eq.5}$$

where V is the calibration volume, T is the calibration temperature and ΔT its variation during the calibration time. The second term represents the apparent leak due to a small pressure change, Δp, and the third represents the apparent leak due to the temperature drift, ΔT. The control of Δp is intrinsic to the process while the control of ΔT is done by maintaining the whole calibration system inside a double-walled box with water flowing at a controlled temperature. Nevertheless, these quantities should be monitored to validate the calibration and for the uncertainty budget. Traceability of the flow rate is given by the pressure, time, and displaced volume. The only required absolute quantity is the pressure.

An embodiment of the calibration device used in the present work is depicted in Fig. 3. The pressure gauge is a DRUCK TERPS 8100 barometer version 700–1300 mbar. The piston is a 1 mL gas tight SGE syringe connected to a NE-500 OEM syringe pump. The volume increase produced by 1000 steps is about 28 μL, ascertained by a calibration. As the syringe is consistently used in the expansion mode, it is manually returned to its initial position, requiring about 400 steps to overcome mechanical hysteresis before initiating any new calibration. The temperature is monitored inside by three Cr–Al thermocouples connected to Fluke 1560 Black Stack Thermometer Readout while it is controlled by a Julabo F25-ED Refrigerated/Heating Circulator. Connections were done with 1/8-inch stainless steel tube with Swagelok fittings and valves.

The whole system is controlled by a LabView computer application which also measures the time. Once the calibration is started, the pressure is continuously read. Upon the detection of an increased pressure produced by the reference leak under calibration, the stepper motor

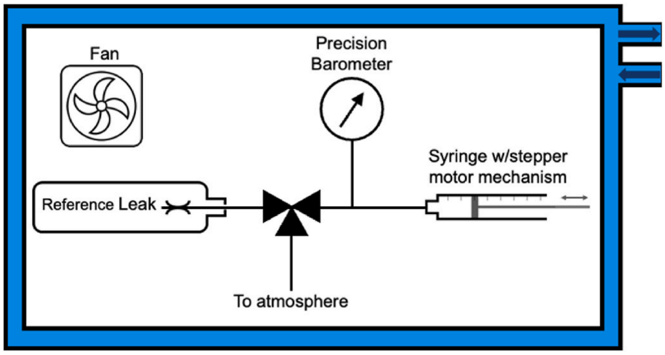

Fig. 3. Calibration instrument for reference leaks based on a constant pressure gas flowmeter.

of the syringe pump expands the volume by a predefined number of steps. For lower leak rates, this is typically a single step, while for higher rates, it can be up to 30 steps. The temperature is also continuously monitored so if it changes more than a predefined amount the calibration is cancelled. The calculated leak rate using the Eq. (4) is plotted in real time. As the time progresses, its dispersion decreases until a well stable quantity is achieved. If the leak rate does not converge, the calibration is suspended and restarted after correcting possible causes.

The calibration time is a function of the leak rate. Normally a volume variation greater than 2000 steps ($\Delta V > 56$ μL) is required to achieve good accuracy. For a leak of 10^{-5} Std cm^3/s this leads to a calibration time of 5800 s (over 90 min). Thus, in the lower end of leak rate an entire night is normally required, while in the upper end, a few minutes are enough. The use of a smaller syringe is a suitable option to reduce the calibration time for the smaller leaks.

3.2. Uncertainty budget

The accuracy of calibrating very small quantities is generally diminished. Deviations from ideal conditions become significant, contributing to an increased uncertainty in the calibration. However, for the present application, high accuracy is not essential. It is important to note that leak detection aims to ensure safety rather than providing a precise measurement of any leak. Consequently, acceptance criteria often include substantial safety factors to guarantee appropriate measures are taken in the event of a leak, prioritising safety over minute uncertainties.

In the present method the uncertainty sources are understood from Eqs. (4) and (5). In the ideal case of Eq. (4), $\Delta p = 0$ (constant pressure) and $\Delta T = 0$ (no temperature drift during calibration time), the uncertainty contributions are those from the volume change ΔV, the absolute pressure, and time. However, the ideal conditions cannot be guaranteed beyond the instruments' resolution, therefore at least such contribution should be accounted for. That means that Eq. (5) should be used, combining variables supposed to be constant with their variations. This equation encompasses not only variations in the absolute pressure and temperature but also accounts for the effect of the dead volume. While p and Δp refer to the same quantity (in the same way as T and ΔT), their contribution to the combined uncertainty should be carefully examined. For the absolute quantity, uncertainty comes directly from instrument calibration, which describes its closeness to the true value. Depending on several factors, the instruments' uncertainty can be as small as its resolution or much higher. However, the uncertainty on measuring the variation of that same quantity is better assessed from repeatability experiments obtained under consistent conditions rather than external calibrations. For instance, if a high-resolution barometer has no scattered readings of the same pressure and a smooth change in response to variations, then the uncertainty on reading variations of pressure is close to its resolution. Therefore, we can control the stability of pressure within the instrument resolution, regardless of how far it may be from the true value given by the external calibration. The same applies to the temperature.

The present method can afford a large contribution to the uncertainty of p but not as large for Δp, which should be kept close to 0.1 mbar. The same applies to T and ΔT in which the contribution of the latter should be close to 0.1 K. Thus, we should take the absolute quantities (p, V and T) and its variations (Δp, ΔV and ΔT) as separate variables, each of them having their own uncertainties.

In the present calibration set-up, the pressure gauge and the thermometer underwent external calibration. The syringe was also calibrated for volume variation in steps that are multiples of 1000. The uncertainty contribution of these measurands was given by the calibration certificates. The uncertainties for Δp and ΔT were ascertained from experiments measuring the dispersion of a constant p and T values. For time, an uncertainty of 1 s was taken, which any computer can easily surpass. The dead volume V is difficult to measure since it is the sum of many small volumes of tubes, valves, gauge, and syringe. Therefore, it was measured in situ using a known reference leak (calibrated elsewhere) and following the pressure increase.

An extra component contributing to the uncertainty is derived from repeated measurements on the same reference leak, typically involving three repetitions. This process averages random errors and fluctuations, which are then incorporated into the overall uncertainty budget. Table 2 provides a summary of the uncertainty contributions for each variable, along with the overall budget for the calibration of one of the produced hydrogen leaks. The sensitivity coefficients were obtained by the derivation of Eq. (5) regarding each variable. Other contributions such as tightness of the calibration system or pressure gradients are considered negligible and therefore not accounted for.

As expected, the most critical contributions are those related with the precision of maintaining the ideal conditions and in measuring the volume change. The first two contributions in Table 2 may be reduced by reducing the dead volume. The uncertainty in measuring the absolute quantities of V, p and T is less relevant as is in measuring the time. However, in this particular example, the uncertainty of p is still relatively high, which is explained by the high uncertainty associated with the standard used in the barometer calibration. The repeatability is typically less than 1% above 10^{-5} Std cm^3/s (relative to the average value) but in the lower end increases up to approximately 10%.

3.3. Results and discussion

Table 3 shows the specifications of the three reference leaks manufactured for hydrogen covering the intended 2 orders of magnitude. The restriction made with compressed PEEK was about 6 mm x ø 2.5 mm introduced inside a 1/8-inch tube. Its adjustment was easy until the decade of 10^{-5} Std cm^3/s tested by spraying He. Achieving a leak rate in the 10^{-7} decade required some patience. Even at the target leak rate, the time required to get a table flow was very short (of a few seconds) confirming that gas was flowing through channels, not permeating the polymer.

The leak with the lowest flow rate was built with a small, exposed area of PTFE following design B of Fig. 2 while other two were based on the design B. The leak rate closely followed the permeation area of the tube for the same pressure, confirming how easy it is to adjust the leak rate based on the tube area. In these restrictions the gas flow took a few hours to reach a stable value, as it is typical of permeation in dense membranes.

All fittings were metal sealed, avoiding the use of O-rings or other polymers which could permeate hydrogen. Only the filling valve had a polymer bonnet.

The depletion rate at the higher end reference leak is 20%/year meaning that one year after calibration it will be 6.4×10^{-5} Std cm^3/s. This depletion rate could be decreased by increasing the filling pressure combined with a shorter or thicker PTFE tube. Another option would be just increasing the volume of the reservoir. After a few years this reference leak should be refilled prior to calibration. Since the leak rate scales linearly with the reservoir pressure, the gauge reading is useful for correcting the flow rate and to define the time for refilling.

It is known that polymers permeate more at higher temperatures [21]. On the other hand, 'open' restrictions are relatively insensitive to temperature. Thus, it is relevant to measure the temperature dependence of the flow rate of the produced reference leaks. This was done by changing the temperature inside the calibration chamber about 5 K higher and lower than the ambient temperature (≈23 °C). From the flow rate measured at these 3 different temperatures the temperature coefficient was calculated as 1.7 %/K for the conductance leak and 4.7%/K for the PTFE restrictions. This means that the flow rate of the leak of 1.78×10^{-5} measured at 23 °C will be 1.96 at 25 °C and 1.60 at 21 °C. If accurate measurements are needed the flow rate can be corrected by the temperature based on the measured coefficient of the leak.

The produced reference leaks were used to test two hydrogen leak

Table 2
Uncertainty budget for the reference leak of 1.78 × 10^{-5} Std cm^3/s.

Quantity	Value	Sens. coefficient $c_i = \left\|\frac{\partial Q}{\partial x_i}\right\|$	Contribution	Distribution & (degrees of freedom)	Divider	Uncertainty contribution	Relative contribution
p, total pressure	999.93 mbar	$\left\|\frac{\Delta V}{\Delta t}+\frac{V\Delta T}{T\Delta t}\right\|$	2.28 mbar	Normal (50)	1	4.20×10^{-8}	5.74%
Δp, maximum pressure change	0.05 mbar	$\left\|\frac{V}{\Delta t}\right\|$	0.05 mbar	Rectangular (50000)	$2\sqrt{3}$	3.83×10^{-8}	4.77%
V, dead volume	12507.69 µL	$\left\|\frac{\Delta p}{\Delta t}+\frac{p\Delta T}{T\Delta t}\right\|$	669.12 µL	Normal (50)	1	3.11×10^{-8}	3.14%
ΔV, volume change	84.68 µL	$\left\|\frac{p}{\Delta t}\right\|$	0.38 µL	Normal (50)	1	8.02×10^{-8}	20.93%
T, temperature	296.28 K	$\left\|-\frac{1}{T^2}\frac{p\,V\Delta T}{\Delta t}\right\|$	0.15 K	Normal (50)	1	2.27×10^{-10}	0.00%
ΔT, max. temp. change	0.05 K	$\left\|\frac{p\,V}{T\Delta t}\right\|$	0.05 K	Rectangular (50000)	$2\sqrt{3}$	1.29×10^{-7}	54.36%
Δt, calibration time	4710 s	$\left\|-\frac{\Delta p\,V}{\Delta t^2}-\frac{p\Delta V}{\Delta t^2}-\frac{P\,V\Delta T}{T\Delta t^2}\right\|$	1 s	Normal (50)	1	3.94×10^{-9}	0.05%
rep, repeatability	–	1	1.99×10^{-7} Std cm^3/s	Rectangular (50000)	$2\sqrt{3}$	5.82×10^{-8}	11.00%
Expanded uncertainty							k = 2.00
Result							1.78×10^{-5} ± 1.89%

Table 3
Main characteristics of manufactured artefacts; all leaks were made with 0.3 L reservoir.

Flow rate (Std cm3/s)	Type	Restriction	Filling pressure (barg)	Depletion rate (%/year)
1.34×10^{-6} ± 10%	Permeation	Design B Area = 6.3 mm^2 Thickness = 1 mm	8.5	1.5%
1.78×10^{-5} ± 3%	Permeation	Design C Area = 207.3 mm^2 Thickness = 1 mm	11.5	14%
8,02 × 10^{-5} ± 1%	Permeation	Design C Area = 386.4 mm^2 Thickness = 1 mm	38.0	20%
7,55 × 10^{-6} ± 3%	Conductance	Design A PEEK compressed powder	41.0	3%

detectors - an Adixen ASM140D and an INFICON Sentrac STRIX. The ASM140 was the same leak detector described before used to adjust the leak rate. The gas mass at the mass spectrometer can be selected between He and H_2 and can be used in the vacuum mode (leak flowing into vacuum) and in sniffer mode, with a probe sucking gas at 1 cm^3/s. The Sentrac is a detector based on a solid-state sensor, highly selective for H_2. Although it has no pump, it offers a reading in flow rate and concentration units. Both have detection limits down to 10^{-6} Std cm^3/s with proper zeroing.

The testing procedure was as follows. The probe was positioned at the reference leak outlet while the detector reading was monitored. The probe orientation was adjusted until a maximum reading was obtained. The instrument was calibrated with the reference leak of 1.34 × 10^{-6} Std cm^3/s following the manufacturer instructions and then the other two leaks were assessed by 3 operators in the same day, under the same environmental conditions. The results are plotted in Fig. 4. Each value presented in the graph is the average of 3 consecutive measurements of the same leak carried out by the same operator, with error being one standard deviation above and below the calculated value.

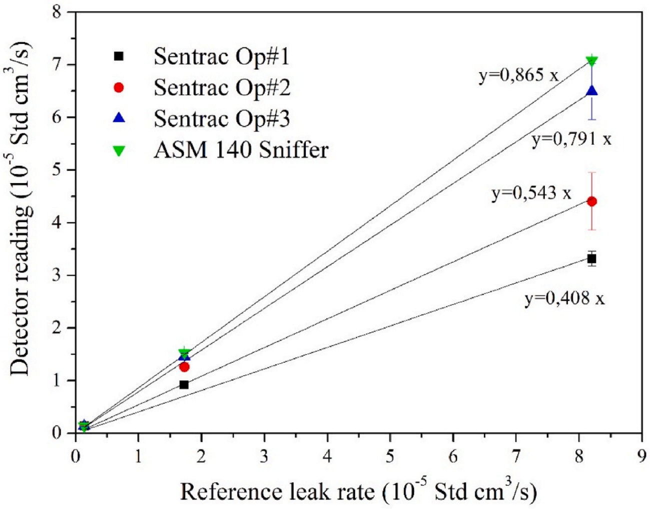

Fig. 4. Testing of two hydrogen leak detectors. Both were calibrated for the leak rate at 1.34 × 10^{-6} Std cm^3/s. All reference leaks were measured 3 times by 3 different operators. For the ASM140D the standard deviation was very small, so error bars are hardly visible.

Both instruments did detect the smallest leakage without difficulty. However, it was noticed that the reading of the Sentrac detector was more scattered and very dependent on the operator. This is something the manufacturer also mentions in the instrument's manual, as readings are influenced by the way the probe is approached to the leak source. Unwanted air flows around the leak testing location can also help explain the scattered results, though the testing conditions mimic real-life use as closely as possible. The fact that gas is pumped into the probe of ASM140D made it very easy to get reproducible readings, showing that it is less sensitive to its position and orientation. Despite both instruments being quite linear, they presented a reasonable deviation from a slope of 1 which is expected whenever a single point calibration is used. However, the ASM140D detector, when tuned for He shows the slope of 1.00 when tested with reference leaks of that gas, both in vacuum and sniffer modes. These results mean that the calibration of these detectors for hydrogen is valid in a narrow range of leak rates around the calibration point, being more critical for the Sentrac detector.

4. Conclusions

Reference leaks are the adequate choice to test hydrogen leak detectors and to ensure traceability every time ‘small’ leak rates need to be measured. These artefacts can be produced in the range of 10^{-6} to 10^{-4} Std cm^3/s with high portability and an acceptable depletion rate. Reference leaks offer a quasi-constant flow rate over many years and are robust and safe for field and laboratory use. A constant pressure gas flowmeter, as the one which is described, is a suitable calibration technique for the calibration of reference leaks in this range, offering sufficiently low uncertainty.

Reference leaks can be used in different ways: (1) to certify the sensitivity of the leak detector under standard conditions in a laboratory, (2) to further test leak detectors for linearity, repeatability, reproducibility, response time, and (3) in the field to make any leakage measurement traceable to SI units. The latter is done just by correcting the measurement of any leakage by the ratio of the reading of the calibrated leak by the reference leak rate given by the artefact.

As these reference leaks have pressured reservoirs, air transport has constraints. Therefore, it is important that more laboratories prepare to offer calibration services as more hydrogen leak detectors are expected to start being used soon for leak detection in hydrogen and hydrogen-enriched natural gas pipelines.

CRediT authorship contribution statement

Orlando Ferreira: Writing – original draft, Writing – review & editing. **Ana Fonseca:** Writing – original draft, Writing – review & editing. **Carolina F. Adame:** Writing – original draft, Writing – review & editing. **Nenad Bundaleski:** Writing – original draft, Writing – review & editing. **Rod Robinson:** Writing – original draft, Writing – review & editing. **Orlando M.N.D. Teodoro:** Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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