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# A comparative study of odorants for gas escape detection of natural gas and hydrogen.

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- 10 Keywords: Hydrogen, Odorant, Gas Network, Olfactory Testing

#### 11 Abstract

- 12 Decarbonising the residential heating and cooking sector is essential to meet national and international
- 13 carbon emission reduction targets. Hydrogen has been identified by the scientific community, industry,
- 14 and policy makers as part of the solution to this challenge. Hydrogen has been used for decades in many
- 15 industries, formerly making up approximately 50% of the Town Gas used for heating and cooking in UK
- 16 homes in the mid 20<sup>th</sup> century. It is now crucial to ensure safety regulations are met, and public
- 17 acceptance gained, before hydrogen can start being used for residential heating. Demonstration projects
- 18 require hydrogen distribution networks to be odorised. This study examines the use of sulphur-based
- 19 odorants, which are currently in use in the UK and Europe to odorise Natural Gas, to be used in a 100%
- 20 hydrogen gas demonstration network in the UK. We undertook a comparative testing programme to
- 21 evaluate the escape detection properties of odorised hydrogen against odorised methane and natural gas.
- 22 This comparative approach will help address the question asked by UK and EU regulators: is hydrogen
- 23 'as safe as' natural gas? The results show that untrained participants can identify an escaping gas odorised
- 24 with Odorant New Blend and standby odorant 2, in hydrogen, natural gas or methane, at the regulatory
- threshold of 1% gas in air. These results contribute to the safety-case of H100 led by SGN.

#### 26 Introduction

- 27 Hydrogen is currently being considered to support the decarbonisation of the energy systems which are,
- 28 at present, overly reliant on GHG emitting natural gas. Ensuring that hydrogen is 'as safe as' natural gas is
- 29 a critical requirement for this transition to happen (Kopasz, 2007). Odorising hydrogen to allow escape
- 30 detection, without artificial sensors and training, is paramount in achieving the safety standards required
- 31 for domestic use. Here we present the need for hydrogen in the current energy system and what it means

- 32 for innovative projects like H100 led by SGN for which this work was carried out. We then follow by an
- 33 overview of the history of the odorisation of gases, and then highlight the remaining knowledge gaps that
- 34 need addressing to ensure that the rate of hydrogen uptake allows decarbonisation targets to be met.

#### 35 Hydrogen in a changing Energy System

36 Hydrogen gas has been identified as a significant contributor to achieving a low-carbon future. Hydrogen 37 has been proposed as an alternative zero-carbon energy carrier, which can be converted to heat or 38 electricity, with the potential to be easily stored and transported (Pudukudy, Yaakob, Mohammad, 39 Narayanan, & Sopian, 2014). Hydrogen would also contribute to increasing the security of the energy 40 system by reducing the dependency on fossil fuels (Sheffield & Sheffield, 2007). Most importantly it 41 would act as a carrier allowing energy to be transmitted and used across the transport, heat, industry and 42 power generation sectors (Staffell et al., 2019). Hydrogen could indeed allow the decarbonisation of the 43 heat and transport sectors, which have proved challenging to decarbonise in comparison to electricity 44 generation (Staffell et al., 2019). In the UK, for example, which relies on natural gas to heat 84% of its 45 households, the gas emissions from the residential sector has reduced by only 16% from 1990 levels 46 (BEIS, 2019). This illustrates that the rate of decarbonisation of heating needs to be increased rapidly 47 (Staffell et al., 2019). Not only would hydrogen offer a way forward in speeding up the decarbonisation of 48 the residential sector, but it would also offer end users the opportunity to keep using heat in a familiar 49 and accepted way e.g. through combustion boilers and cookers, similar to the natural gas products in use 50 today (Dodds & Demoullin, 2013). Hydrogen would also offer, with some network reinforcement, a 51 decarbonised future to the vast national and international infrastructure used to deliver gas which has 52 been upgraded over the past 50 years (Dodds & Demoullin, 2013).

#### 53 Hydrogen 100 Project – Residential heating and cooking through a 100% hydrogen

#### 54 network

- This work was commissioned by SGN and supports the safety case of the 'Hydrogen 100' innovation
  project. SGN is a UK gas distribution network operator. The Hydrogen 100 project seeks to demonstrate
- 57 the feasibility of supplying 100% hydrogen to 300 selected homes which could include small businesses.
- 58 The project will ensure that new 100% hydrogen compatible appliances are installed and a new hydrogen
- 59 distribution network is built. We note that although a wider transition to hydrogen use would rely on both
- 60 new and existing infrastructure, this demonstration project relies on new assets to reduce risk and
- 61 uncertainty whilst gathering knowledge and experience. The work presented in this study investigates
- 62 whether odorised hydrogen releases within a conceptual domestic space would be as readily detectable as
- 63 a release from odorised natural gas. The Hydrogen 100 project includes a comprehensive investigation of
- 64 hydrogen delivery through a new polyethylene distribution network. Further investigations related to
- 65 odorants are being undertaken including physical testing of material exposed to odorised natural gas and
- 66 hydrogen.

#### 67 Brief history of gas odorisation

- 68 Mining has historically been an industry where exposure to the hazards of odourless combustible gases
- 69 was frequent and deadly. When gas started to be used more readily in the 19th century in urban settings
- 70 the idea of odorising this gas, before use, was proposed by Julius Quaglio (in 1880) in Germany (Fink,
- 71 2015). Although gas from natural sources often contains impurities providing a natural odour, processing
- 72 techniques increased the odourless character of some pure gases like methane, carbon monoxide, carbon
- 73 dioxide and hydrogen, making them more dangerous. Natural gas has been odorised for more than a
- 74 century (Kilgallon, Gilfillan, Haszeldine, & McDermott, 2015). The odorisation of natural gas from
- 75 distribution networks became a legal obligation following the 'New London School' accident in Texas
- 76 (1937), which claimed the lives of 294 people (Kopasz, 2007). Odorisation is regulated because the
- 77 primary component of natural gas, methane, is colourless and odourless. Since the same is true for
- 78 hydrogen, artificial odorisation using an odorant compound would be required to meet regulations.
- 79 Still to this day, in order to deliver gas to customers via a distribution network, gas needs to be odorised.
- 80 Odorisation is a legal requirement in many countries because it is deemed an essential safety feature
- 81 (Dodds & Demoullin, 2013; Puri, 2006). Indeed, most healthy people untrained in olfactory detection will
- 82 be able to detect the distinctive smell associated with a gas escape due to the now widely enforced
- 83 odorisation practices.

#### 84 Research gap in hydrogen network odorisation assessment

- 85 Significant research has been undertaken on the odorisation of natural gas in pipelines. Some key points
- to consider with gas odorisation are the detectable limits of the gas odour, the type of odorant used (e.g.
- 87 sulphur based, acrylate), the odorisation technique, and the monitoring system used to ensure that
- 88 odorants meet the regulatory thresholds. These aspects are reviewed in Fant (1993).
- 89 The literature highlights both the importance of odorising hydrogen (Brewer, 1978) whilst acknowledging
- 90 that the odorants might not behave in the same way in hydrogen as they do in natural gas. This is
- 91 primarily due to the different chemical and physical properties of hydrogen (Dodds & Demoullin, 2013;
- 92 Kopasz, 2007). The chemical compatibility of sulphur based odorants with hydrogen during piped
- 93 transport has been demonstrated by the Health and Safety Executive of the UK (JP Hodges, Geary,
- **94** Graham, Hooker, & Goff, 2015).
- 95 However, there remains a lack of reported investigation into the physical and olfactory properties of high
- 96 purity hydrogen and odorant mixtures. This lack of investigation could hinder the progress of crucial
- 97 demonstration projects needed to prove the use and deployment of hydrogen at scale. To date most of
- 98 the focus on hydrogen odorisation has been placed on the end uses. In particular, fuel cells used to
- 99 produce electricity from hydrogen (de Wild, Nyqvist, de Bruijn, & Stobbe, 2006; Dodds & Demoullin,
- 100 2013; Imamura, Akai, & Watanabe, 2005; Kopasz, 2007). This is understandable since commonly used
- 101 sulphur based odorants are toxic to fuel cells, and fuel cells are likely to become a critical end use for

- 102 hydrogen (Staffell et al., 2019). Hence, a research focus to date has been placed on the desulfurization of
- 103 odorised gas (Kim et al. 2007, Bae et al. 2009, Oshima et al. 2020). However, our study addresses the lack
- 104 of investigation into the olfactory response to odorised hydrogen compared to natural gas, for an
- 105 equivalent end use aimed at combustion appliances. This work complements a previous study by Mouli-
- 106 Castillo et al. (2020) which investigates the likely olfactory characteristics of odorised hydrogen delivered
- 107 to consumers via a distribution network. The Mouli-Castillo et al. (2020) investigation focused on
- 108 applying standardised olfactory tests to odorised hydrogen. This method provided quantitative
- 109 information, using reproducible tests, but not a direct comparative assessment with odorised natural gas.
- 110 This comparative testing is important since the UK and EU regulators have sought demonstration (via
- 111 comparative testing) that hydrogen is 'as safe as' the natural gas currently in use (HyDeploy website and
- (IRC, 2013)). In this study we report, for the first time, a set of comparative tests undertaken by Kiwa
- 113 Gastec on odorised hydrogen, methane and natural gas from the UK network. We discuss the findings in
- the context of the wider Hydrogen 100 project, as well as the 'as safe as' approach sought by the
- 115 regulators.

#### **116** Odorisation Practices in the UK

117 In this section we briefly introduce the regulations and standards governing gas odorisation practices in

- 118 the UK. In the UK, any gas supplied to end users from a network which has a pressure of 7 bar gauge or
- 119 below should be odorised (Gas Safety (Management) Regulations, 1996).
- 120 The gas should be odorised to impart an odour with an intensity of 2 on the Sales scale (Sales, 1958), that
- is a 'medium odour'. This will allow a gas escape to be detected by the population at 20% of the lower
- 122 flammability limit, which is equivalent to about 1% gas in air concentration for both natural gas and
- 123 hydrogen. In that sense odorisation is designed and regulated to provide warning prior to reaching
- 124 flammable gas mixtures. Hence this study focuses on gas detectability rather than explosion risk, which is
- an important topic in its own right and is being actively investigated (e.g. Sinha et al., 2019; Lowesmith et
- al., 2009, Makarov et al., 2018). ISO 13734:2013 presents the general characteristics of an effective
- 127 odorant:
- 128 a) The gas odorant should have a strong odour at very low concentration, b) The odour character of the odorant needs to be unpleasant, distinctive and not confusable with 129 130 other frequently occurring odours so that it is unmistakably associated with a gas escape, c) The odour character should be the same at different dilutions of natural gas with air, 131 d) The odorant should be sufficiently stable during storage and when mixed with natural gas, 132 The volatility of the odorant should be high enough so that the odorant does not appreciably 133 e) 134 condense under the conditions (temperature and pressure) existing in the pipeline system, Evaporation of the gas odorant should not appreciably leave residues, 135 f) g) The odorant should be useable at low temperatures, when required, 136 h) The combustion of the odorant should not leave significant solid deposits, 137 138 i) The addition of the odorant to natural gas should not make the resulting gas harmful, 139

- 140 Currently demonstration projects, which are designed to underpin and support the uptake of hydrogen as
- 141 a decarbonisation technology, are required to demonstrate that hydrogen can be used in a way which is 'as
- 142 safe as' natural gas is today (HyDeploy, 2019). We have formalised this approach into two research
- 143 hypotheses:
- The odorants currently used with natural gas (generally sulphur based compounds) will be as
   effective when used with hydrogen.
- 146 2. Very small escapes of hydrogen are detectable in the same way as an escape of natural gas in a147 comparable room space.
- 148 These were tested through a series of comparative olfactory experiments that provided quantifiable,
- 149 verifiable, and comparable data on the olfactory response of human participants to both 1) odorised
- 150 hydrogen and 2) natural gas.

#### 151 Methods

152 This section details the experimental setup, choice of participants, the rules the participants had to follow,153 and finally the experimental matrix presenting the tests performed.

#### **154** Experimental Setup

The experimental setup was designed to allow control of as many parameters as possible to ensure
reproducibility of the experimental conditions. The various elements of that setup are described below
and visualised in Figure 1.

- 1581) An enclosure made of timber and heavy-duty polythene sheets. The dimensions of the enclosure159were 3 m wide by 6 m long and 3 m high, giving a total volume of 54 m<sup>3</sup>. These dimensions are160representative of  $a \approx 25 \text{ m}^2$  living room (with a floor to ceiling height of 2.5 m), which was161typical for the 1970's when domestic housing was converted to natural gas, and was consistent162with the standards of the time (LABCWarranty, 2019; Park, 2017). It is deemed appropriate to163use this comparative basis, as it is still representative of the type of UK housing likely to use gas164heating.
- 165 2) An extraction system was installed. It comprised two extraction hoods installed outside the
  166 enclosure above the doors, and an extraction point inside the enclosure. All extraction points
  167 were connected to an extraction duct leading outdoors. The system was design to clear gas from
  168 the enclosure, the door area, and the waste gas from gas chromatographs. This ensured that the
  169 space could be cleared from any gas prior to initiating each experiment i.e. resetting to baseline
  170 conditions.
- 171 3) A system to mix pure gas with an odorant rich gas mixture, and then inject it into the enclosure172 was designed. Injection in the range of 0.01 to 50 litres per minute could be used. The system

- was designed to mix un-odorised gas with odorised gas to reach the 2 part per million volume
- 174 (ppm) odorant concentration target (discussed below) in the injected gas stream.
- 4) A sampling system was put in place which allowed a continuous and controlled extraction rate to
  be set for each of the sampling points. This ensured a fresh sample was always available and that
  there was no lag between any of the sample lines. Ten sample lines were used in total nine to
  sample the enclosure, and one to sample the air outside to provide a reference sample to ensure
  the accuracy of the equipment.



#### 180

**183** The experimental testing was conducted in a controlled, indoor environment in the Kiwa Gastec testing

- 184 laboratories. This avoided the effects of wind on the dispersion of the gas and allowed rigorous control of
- 185 the gas injection and dispersion, including for the final venting procedure at the end of each test. The
- 186 tests were carried at ambient temperature, representative of dwellings in temperate climates, such as the
- 187 UK. The results might not be representative of poorly insulated buildings in tropical, arid, and polar
- 188 regions.

#### 189 Sampling Procedure

190 Two gas chromatograph analysers (Inficon Micro GC Fusion) were used for measuring the levels of

- 191 methane or hydrogen in the sampled gas in ppm. Each chromatograph used a molecular sieve-type
- 192 column heated to 90 °C with an argon carrier gas injected at 69 Millibar (mbar). The chromatographs
- 193 sampled each line in turn through the multipoint sampling valves and the gas in air concentrations (in
- 194 ppm) was recorded. The analysis process consisted of a short purge with the sampled gas 15 s) followed
- 195 by injection into the column within the chromatograph (100 ms) and then progression of the sample
- 196 through the column (120 s). The multipoint sampling valves were moved to the next desired sampling
- 197 line, and the process repeated. The concentration of the flammable gas in question was then calculated
- 198 from the chromatograph, logged, and graphed in real time for visual verification. Using two

<sup>181</sup> Figure 1: Experimental Setup. The height levels of the sampling points are as follow: Top at 2.7m, Mid at 1.5m and182 Low at 0.3m. The dimensions of the wall vents are 229 x 229 mm.

- 199 chromatographs in conjunction enabled for an offset logging sequence whereby the time delay between
- each sampling point being measured was reduced. The sampling order is presented in SupplementaryTable 1.
- 202 Furthermore, the participants were not made aware of where in the enclosure the lines were sampling
- from. In addition, the participants did not know that the lines and sample points were fixed during thecourse of the experiment.
- 205
- 206 Tested Gases & Odorants
- 207 The gases used in this test programme prior to any mixing were:
- 208 1) Line gas from the local gas distribution network (odorised with odorant NB).
- 209 2) Un-odorised methane (reference fuel G20 with over 99% methane (EU Commission, 2017)))
- 210 3) Un-odorised hydrogen (Grade 4.5, that is, with a purity of 99.995%)
- 4) Odorised methane and hydrogen (provided in bottles at 20 ppm odorant concentration)
- 212 Gases were supplied to the injection rig at a pressure of 0.5 bar. A target odorant concentration of 2 ppm
- 213 was achieved by diluting the odorised gas (at 20 ppm) with the equivalent un-odorised gas according to
- the test specifications (Supplementary Table 3). 2 ppm is the concentration used in the UK gas network
- 215 (Mouli-Castillo et al., 2020). The specification for the odorant and gas mixtures used for the experimental
- 216 work were provided by the National Physical Laboratory, and supplemented their research programme on
- the odorisation of hydrogen for gas distribution networks.
- 218 Odorant New Blend (NB) is in use in the UK. It is used, along with its diluted form (known as Standby
- 219 Odorant 2), by the UK distribution network operator SGN. Odorant THT is an odorant commonly used
- 220 on the European mainland. Odorants using mixes of the compounds tested here are also used in Japan
- 221 (Cagnon, 2011). Therefore, the findings from this study are directly applicable to support the
- 222 development of hydrogen networks in many countries.
- **223** The odorant components used are presented in Table 1.
- 224 Table 1: Odorant composition used in the tested mixtures.

Odorant	Composition
New Blend (NB)	78% tert-Butylthiol, 22% Dimethyl Sulfide
Standby Odorant 2	34% Odorant NB, 64% Hexane
Odorant THT	100% TetraHydroThiophene

<sup>225</sup> 

226 The injection rates used aimed for a nominal gas in air (GIA) concentration inside the enclosure of:

- 227 10,000 ppm (1%) which is the concentration of gas at the maximum level allowed by the
  228 regulator (about 20% of the lower flammability limit).
- **229** 1,000 (0.1%) an order of magnitude lower than the regulatory threshold.
- **230** and 500 ppm (0.05%) 20 times lower than the regulatory threshold.
- 231 This range of concentrations allows for reasonable assessment of gas escape detectability before
- 232 dangerous levels of gas are reached, whilst avoiding 'false alarms' from very low concentrations.

#### 233 Air Tightness

- 234 The air permeability of a 'new build' property was assumed a worst-case scenario (Crowther, Orr,
- 235 Thomas, Stephens, & Summerfield, 2015). An air tightness test was conducted to ensure the experimental
- 236 setup was representative of such worst case scenario. This test measured the enclosure's permeability to
- 237 air. A new build property has an air tightness value of  $10 \text{ m}^3/\text{h/m}^2$  or less (Crowther et al., 2015).
- An approved testing company undertook the testing at 0.5 mbar to EN 13829:2001. The 0.5 mbar
- 239 pressure used for the air tightness test is dictated by the standard and not related to the injection pressure
- 240 used in our tests. The air tightness test results (Supplementary Table 2) show that the test enclosure with
- 241 open vents performed comparably to a new build property. All the olfactory testing described in this
- study was undertaken with the wall vents open to be representative of a new build property.

243

#### 244 Test Programme

245 The test programme was divided into two phases. The first phase aimed to calibrate the equipment and 246 understand the pattern of gas dispersion within the enclosure. These tests were completed using un-247 odorised methane and hydrogen, and enabled the determination of injection flow rates that would lead to 248 the targeted gas in air concentration in the second phase. In addition, these tests served to test various

- sampling locations in the horizontal and vertical plane within the enclosure to ensure sampling locations
- 250 were representative and were not biased towards any potential gas accumulations (e.g. in the corners of
- the enclosure). After each test, the enclosure and the space around it, were fully ventilated using the
- extraction system.
- 253 Phase 2 of the experimental programme involved tests using natural gas (line gas), odorised hydrogen,
- and odorised methane. At the start of each experiment, the enclosure was setup in the same manner. The
- wall vents remained open, the centre vent on the extraction system was shut, and an integrity check was
- **256** performed on the gas injection and sample lines. The extraction vents from above either end of the
- enclosure were left open for the duration of the test to allow for the extraction of any escaping gas
- 258 (including waste gas from the chromatographs).
- Once the enclosure setup was completed, the test flow rates of both the odorised gas at 20 ppm, and theun-odorised gas, were set using the mixing rig (Supplementary Table 3). Once the flow rates had stabilised

- to provide approximately 2ppm of odorant within the un-odorised gas the mixed gas was injected into the
- test enclosure via the open end of a 10 mm copper pipe. In order to simulate a domestic space in which
- 263 no active mixing of the volume would occur, it was decided not to homogenise the gas mixture inside the
- enclosure. This implied that the actual gas concentrations inside the enclosure would vary (hence the nine
- sampling points). The reference value of the 'gas in air concentration' (GIA), which was used to set up
- the injected gas flow rate, was located at the centre of the enclosure (see curve labelled 'Mid B' in the
- results section).
- During the gas injection phase of the test, 'sniff tests' were carried out at specified time intervals using the 268 269 sampling ports (Supplementary Figure 1) which were connected to the ten sampling lines. Each sniff test 270 lasted a few seconds before the participant left the test area. Each participant was a voluntary Kiwa staff member untrained in olfactory assessment. They were asked to smell each of the sample ports in turn and 271 272 to record whether they could detect a smell. If a smell was detected the participant was asked to rate the intensity of the smell using the following scoring system of 1 to 5, otherwise a score of 0 was attributed. 273 274 The gas was considered detectable when 50% or more of the trial participants detected a smell on a given 275 sample line. The scoring system was based on a recognised odorant detection and perception scale; used
- 276 for air monitoring and odour science (IAQM, 2018; Nimmermark, Schmidt, Jacobson, & Gay, 2005).
- 277 1) Very faint, may be identified as a gas escape
- 278 2) Faint but identifiable as a gas escape
- **279** 3) Easily detectable and easily identified as a gas escape
- **280** 4) Strong and easily identified as a gas escape
- **281** 5) Very strong/unpleasant easily identified as a gas escape
- Five minutes after the start of injection the first sniff test was performed. This was followed by one every 15 minutes during the injection period. The last sniff test was performed following the cessation of injection, once the concentrations had stabilised around the target level for that test. This final sniff test usually occurred 10 minutes after the stop of injection. Following the sniff tests, the participants were asked to complete a walkthrough of the test enclosure.
- 287 The walkthrough was designed as follows: each participant entered the enclosure through the door
- 288 located at the opposite end to the injection point. They then walked (as a group) through the enclosure
- towards the injection point and exited the enclosure through the door located closest to the injection
- 290 point (Figure 1). The walkthroughs lasted approximately 15 seconds each. Following the walkthrough, the
- 291 participants were asked to comment on the strength of the odour inside the enclosure. The same scale as
- the sniff test was used. In addition, participants were asked to indicate where the first odour was detected.
- 293 One of four locations could be indicated: 1) as soon as the door opened before entering the enclosure, 2)
- as soon as they entered the enclosure, 3) midway through the enclosure, 4) at the injection point.

- 295 The doors of the enclosure were kept closed until the end of the test (except to let the participant exit and
- enter the enclosure). As the focus of the study is placed on the detectability of gas escapes, the tests were
- 297 completed after the end of the walkthrough and no assessment of the dissipation of the gas in the
- 298 enclosure was conducted. Once the test had been completed the enclosure was vented to the outside
- **299** using the central vent of the extraction system (Figure 1).

#### 300 Trial Rules

- 301 This section describes the rules that the participants had to follow during the tests. Safety procedures are
- 302 not described here in detail, only the rules pertaining to the scientific validity of the experiments. A
- 303 complete risk assessment was however carried out to ensure the safety of the participants and the trial
- 304 operators. Key safety measures which should be mentioned are that 1) the flammable gas/air mixtures
- within the test facilities were continually monitored and never exceeded 1% gas in air (GIA), 2) potential
- 306 sources of ignition were not allowed in the enclosure, and 3) any potentially unaccounted for odorant risk
- 307 was mitigated by rotating participants, exposing them to odorised gas for only seconds at a time, and
- **308** asking them to vacate the test area immediately after each test.
- 309 The participants were not qualified in olfactometry and can be described as 'naïve' from that standpoint.
- 310 It should be noted that olfactory literature indicates that increasing age tends to reduce olfactory
- sensitivity, whilst the effect of gender on olfactory sensitivity depends on several factors including the
- study, odorant compound tested, and the test task performed (Bliss, Schulz, SENGER, & Kaye, 1996;
- 313 James Evans, Cui, & Starr, 1995; Klimek, Gudziol, Owen, Pauli, & Hummel, 2000; Nguyen, Rumeau,
- Gallet, & Jankowski, 2016). To ensure any that age and gender factors were captured in the study, both
- female and male participants were selected over three age groups 1) under 30 years old, 2) 30 to 50 years
- 316 old and 3) over 50 years old. For each test a mix of males, females and ages was ensured.
- 317 To evaluate the public's response to an escape of odorised gas, standards cannot be used as they require
- 318 olfactory experts rather than untrained members of the public (CEN, 2003). Using untrained participants
- 319 presented a methodological risk since the participants might not have constituted a representative sample
- 320 of the wider population. This could have introduced bias. To account for this bias, the research was
- 321 designed as a comparative study, assuming that any bias from the untrained participants would apply
- 322 equally to all gases and odorants tested. Further confidence can be had by comparing the findings with
- 323 standardised tests' results, although these usually lack the comparative element added by this study (see
- 324 discussion section) (Mouli-Castillo et al., 2020). This allows a useful comparative analysis. Such
- 325 comparative assessments are needed to develop quantitative risk assessments (QRAs) for demonstration326 projects.
- 327 To guarantee that no cross-contamination or 'nose blindness' occurred for the participants, the following328 procedures were enforced:

- The location of each sample point within the enclosure was not communicated to the participant.
   This removed the opportunity for the participants to pre-assume a particular gas concentration,
   and therefore bias their judgment (e.g. hydrogen concentrations are higher closer to the ceiling,
   therefore odour should be greater too).
- 333 2) The participants did not know the gas injection rate and the target GIA (ppm) concentration.334 This avoided any expectations as to whether or not an odour 'should' be detectable.
- 3) For the entire duration of the test the participant were prevented from accessing the zone where
  the cylinders with the concentrated odorised gases (at 20 ppm) were stored. This avoided any
  exposure to the odorant via a gas escape from the regulator, or from the valve of the cylinder.
- 338 4) The participants were instructed to leave the test area immediately after each experiment (sniff339 test or walkthrough).
- 340 5) Participants were rotated regularly and limited to the number of tests which could be conducted341 in a day.
- 342 6) Between 3 and 4 participants took part in each test.

#### 343 Experimental Matrix

- 344 The experimental matrix used for the phase 2 of the testing can be found in the Supplementary Table 3.
- A total of 18 tests were carried out. In test 1,2, and 3 it was observed that no odorant was detected at all.
- 346 This was attributed to the odorant being retained by the pipework in the initial tests. This is common
- 347 phenomenon and industrial pipes are commonly 'soaked' with odorants prior to being used for
- 348 commercial purposes. For this reason test 1,2 and 3, were repeated as test 6,7 and 13 respectively.

349

#### 350 Results

- 351 The following sections present the results of the Phase 2 tests (presented in Supplementary Table 3) for
- 352 which odorant detection occurred. We also explicitly mention for which tests no detection occurred. For
- **353** each test the following items are presented: the GIA concentration obtained during the test, the time at
- 354 which the first detection via a sniff test occurred, and the time and gas concentration in the enclosure
- 355 when the walkthrough was conducted. The results are presented in subsection for each gas-odorant pair
- **356** tested. Each subsection presents the results for the different concentrations tested.

#### 357 Natural Gas

358 The presence of natural gas (line gas) was detected during the 10,000 ppm GIA test 4 (Figure 2.a), but not359 during the two 1,000 ppm GIA tests 3 and 13.



360

Figure 2: a) Test 4, natural gas (line gas) at a target concentration of 1% GIA. b) Test 4 - Average intensity recordedfor the sniff tests.

363 Following initial detection after 1h05min of the natural gas odour on the sample lines 1 and 4, the odour

364 remained detectable throughout the rest of the test period (Figure 2.b). The greatest odour intensity was

365 usually recorded for sample lines 1 and 2 (the top and middle sample points furthest from the injection

point), and line 4 at the high level in the middle of the enclosure (Figure 2.b).

#### 367 Hydrogen with Odorant NB

- 368 Hydrogen was tested with Odorant NB (the principal odorant used in the UK natural gas network).
- **369** During the 500 ppm, 1,000 ppm and 10,000 ppm GIA tests, gas odour was identified.
- 370 During the 500 ppm experiment, sniff detection scores were variable with a highest intensity of 1. This
- 371 rose to a maximum of 2 during walkthrough (Table 2).
- 372 During the 1,000 ppm and 10,000 ppm experiments (Figure 3 and 5 respectively), once odours were
- 373 detected in the sniff tests, the odour remained apparent for the remainder of the trial period. The
- maximum intensity during the 1,000 ppm sniff test was 3, with an average of 1 (Figure 3.b). This rose to 4
- 375 during the walkthrough of the enclosure (Table 2). The gas smell was first identified in the enclosure at an
- average GIA concentration of about 600 ppm (maximum GIA of about 1,400 ppm Figure 3.a). A smell
- 377 was detected on all sample lines, with lines 1 and 2 (top and mid-level furthest from the injection point)
- **378** perceived to have the highest intensity of smell.



Figure 3: a) Test 7, hydrogen and odorant NB at a target concentration of 0.1% GIA. b) Test 7 Average intensityrecorded for the sniff tests.

382 During the 10,000 ppm experiment, 20 minutes after the start of injection, an odour with an intensity of 2
383 was detected (Figure 4.b). At which point the maximum GIA concentration within the enclosure was
384 ~3,000 ppm, with an average of ~1,000 ppm (Figure 4.a). During the sniff tests the average odour level
385 was 2 (Figure 4.b). This was lower than the recorded value during the walkthrough of the enclosure
386 where an intensity of 4 was recorded by all participants (Table 2). Once again, the strongest intensity of
387 smell was recorded on sample lines 1 and 2, followed closely by line 4 (top position in the centre of the
388 enclosure).



379



- Figure 4: a) Test 5, hydrogen and odorant NB at a target concentration of 1% GIA. b) Test 5 Average intensityrecorded for the sniff tests.
- **393** Hydrogen with diluted Odorant NB (standby 2)
- Hydrogen was tested with hexane-diluted Odorant NB i.e. standby odorant 2, which is used by SGN inthe UK.
- **396** Once tests 5 to 8 had been performed it was determined that due to the intensity of the odorant, and the
- 397 similarity between the standby odorant 2 and Odorant NB, if standby odorant 2 was detected at low GIA

- concentrations, then testing at higher concentrations was not required, since Odorant NB had beendetectable at higher concentrations.
- 400 The presence of gas was not identifiable with standby odorant 2 at 500 ppm GIA concentrations.
- 401 During both the 1,000 ppm sniff tests and enclosure walkthrough, hydrogen odorized with standby
- 402 odorant 2 was reported at a maximum intensity of 3, although the average intensity oscillated between 0
- 403 and 1 (Figure 5.b). Some of the participants identified it as a gas escape in their comments. At the time of
- 404 first detection during the sniff tests, a maximum GIA concentration inside the enclosure of around 1,600
- 405 ppm was recorded, with an average GIA inside the room of about 650 ppm (Figure 5.a). Once identified
- 406 the gas odour stayed evident during the remainder of the sniff tests.
- 407 Once again, the strongest intensity of smell was consistently recorded on sample line 1. Following the
- 408 initial detection, the odour was identified on all the sample lines as presented in Figure 5.b.



409

410 Figure 5: a) Test 10, hydrogen and standby odorant 2 at a target concentration of 0.1% GIA. b) Test 10 Average411 intensity recorded for the sniff tests.

#### 412 Hydrogen with THT

- 413 During the test of hydrogen odorised with odorant THT, gas was identified by the participants during the
- 414 10,000 ppm GIA concentration test (Figure 6 6.a). However, it was not detected for the tests with a GIA
- 415 concentration of 500 ppm or 1,000 ppm.
- 416 The sniff tests conducted during the 10,000 ppm GIA concentration experiment revealed that the
- 417 maximum odour intensity, which could be identified by the participants, was 2 (Figure 6.b). The
- 418 participants also recorded that the smell was unpleasant but not immediately identifiable as a gas escape.
- 419 The odour character was described as "chemically" or "similar to onion/garlic". At the time of first
- 420 detection, 1h05, by sniff tests the maximum GIA concentration within the enclosure was about 8,500
- 421 ppm, with an average of around 5,400 ppm (Figure 6.a). As in most of the previous tests, the highest
- 422 odour intensity levels were recorded on sample lines 1, 2 and 4 (Figure 6.b).

- 423 The odour intensity registered by all but one of the participants during the walkthrough was of 4 (Table
- 424 2). This is higher by two scale points than during the sniff tests. A participant commented that the
- 425 enclosure had a musty odour, whilst only scoring that odour at an intensity score of 1. The participants
- 426 characterised the odour as "chemically" or "very strong onion" or "garlic".





428 Figure 6: a) Test 18, hydrogen and THT at a target concentration of 1% GIA. b) Test 18 Average intensity recorded429 for the sniff tests.

- 430 Methane with NB
- 431 Methane (G20) combined with Odorant NB at 2 ppm was tested. The presence of gas could be identified
- 432 by smell by the participants during the 10,000 ppm GIA concentration test (Figure 7.a). No odour was
- 433 detected for the tests conducted at GIA concentrations of 500 ppm and 1,000 ppm (tests 15 and 16).
- 434 The maximum odour intensity recorded in the sniff tests was a value of 4 (Figure 7.b). The detection
- 435 occurred after 20 minutes of injection (Figure 7.b). The maximum odour intensity of 2 at the time of
- 436 detection during the 10,000 ppm experiment (Figure 7.b). At the point of first detection, the highest GIA
- 437 concentration within the enclosure was approximately 2,000 ppm, with an average of about 700 ppm
- 438 (Figure 7.a). The average odour intensity as indicated on each sample line by the participants is shown in
- **439** Figure 7.b.
- 440 During the walkthrough a maximum odour intensity of 4 was recorded inside the enclosure (Table 2).
- 441 This intensity is consistent with the maximum identified during the sniff tests.





443 Figure 7: a) Test 17, methane (G20) and odorant NB at a target concentration of 1% GIA. b) Test 17 Average444 intensity recorded for the sniff tests.

445

#### 446 Odorant Tracking

- 447 Table 2 displays the walkthrough findings during which gas was identified and ranked on odour intensity.
- 448 It indicates at which location the scent was identified– "Door Open" means the odour was perceived as

the door opened before the participant entered the enclosure.

- 450 The entrance door was furthest from the point of injection. The point of injection was located at the end
- 451 of the enclosure. Odour identification took place at the 'entry to enclosure' (Table 2). This is evidence
- 452 that the odorant persisted within the gas as it passed through the room, or that the concentration of
- 453 odorant within the gas was sufficiently intense to be detectable everywhere within the release area.
- 454 The detection of the various odorised gases during the 'sniff tests' at sample lines 1, 2 and 3 (located
- 455 furthest and closest to the injection point) are consistent with the observation that odorants do indeed
- 456 remain within the hydrogen. It is conceivable that after the odour was identified the participants became
- 457 used to the odour, and thus the lines which were sampled last appeared less intense. In some cases, the
- 458 participants of the experiment were asked to reverse the order in which they checked the sample lines
- 459 (still without knowledge of which sample line corresponded to which sample point), however this led to
- 460 only minor variation in the apparent strength of the odour.

461	Table 2: Odour intensity recorded by participants during the walkthrough of the enclosure at given target locations.
462	The letter does not identify a specific participant.

Test	Participant	Door Open	Entry to enclosure	Middle of enclosure	Point of gas injection
4 - 10,000 ppm Line Gas	А	0	0	4	4
	В	0	0	3	3
	С	4	4	5	5
	D	4	4	5	5
5 - 10,000 ppm Hydrogen NB	А	4	4	4	4

	В	4	4	4	4
	С	4	4	4	4
	D	4	4	4	4
7 - 1,000 ppm Hydrogen NB	А	0	3	3	3
	В	0	3	3	3
	С	0	3	3	3
	D	0	3	3	3
8 - 500 ppm Hydrogen NB	А	0	2	2	2
	В	0	2	2	2
	С	0	1	1	1
	D	0	2	2	2
10 - 1,000 Hydrogen Standby 2	А	3	3	0	3
	В	2	2	0	0
	С	2	2	1	1
12 - 1,000 Hydrogen THT	А	2	2	1	0
	В	0	0	0	0
	С	0	0	0	0
	D	2	2	1	1
17 - 10,000 Methane NB	А	5	5	5	5
	В	4	4	4	4
	С	0	4	4	4
18 - 10,000 Hydrogen THT	А	4	4	4	4
	В	4	4	4	4
	С	1	1	1	1

#### 463 Discussion

- 464 This study tested the two hypothesis that 1) the odorants currently used with natural gas will have a
- similar effectiveness when used with hydrogen, and 2) that the detection of very small escapes of
- 466 hydrogen are detectable in a similar way to a natural gas escape in an equivalent room volume. This
- 467 section discusses how the findings address these hypotheses and outlines the results limitations.

468 The study was designed around the UK's legal requirement that the presence of gas should be readily

469 detectable by smell at GIA concentration of 20% of the lower flammability limit. This equates to around

470 1% GIA for both methane and hydrogen (Gov, 1996). At this 1% GIA concentration, all the tested

471 odorants led to the gas releases being detected by the trial participants. When mixed with either hydrogen

- 472 or methane, both Odorant NB or Standby odorant 2 led to the smell being identified specifically as a gas
- 473 escape at concentrations of 1% GIA. As such, it can be concluded that, under the conditions of this trial,
- 474 the two hypothesis are verified.
- 475 During the hydrogen THT tests the odorant was detected at 1% GIA concentration, but not identified
- 476 specifically as a gas escape by participants. The trial participants being UK residents could explain why
- 477 they did not identify a gas odorised with an odorant primarily used on the European mainland. This result

- 478 suggests how embedded the odour character of gas is in a given population and corroborates the
- 479 observation made by a report for the Health and Safety Executive of the UK (J. Hodges, Geary, Graham,
- 480 Hooker, & Goff, 2015). This illustrates that, should a different odorant to the ones being used today be
- 481 used in future hydrogen networks, the public should be correctly informed and educated to associate the
- 482 new odour character to a gas escape.
- 483 Another observation of note is that odorant NB, currently in use in the UK, was detected at much lower
- 484 concentrations (down to 0.05% GIA) when mixed with hydrogen in comparison with a detection
- 485 occurring at 1% GIA when mixed with methane, or as part of line gas. However, the testing method
- 486 does not allow for the cause of this to be determined with certainty. In addition, the results indicated that
  487 stratification of the gases within an enclosure 3 m high does not negatively affect the detection potential
  488 of a gas escape.
- ioo of a gas escape.
- 489 Additionally, we note that the THT target concentration in the gas was set to 2 ppm as per odorant NB
- 490 and standby odorant 2 in the UK. However, literature suggests that the THT concentration in use in the

491 European mainland are in the range of 3 to 11 ppm (Uni. Of. Miskolc & Hungarian Scientific Society of

- energy Economics, 2008; Zhang, 2019). This could explain why THT appeared to be less easily detectablethan odorant NB.
- 494 Table 3 summarises that, for odorant NB and Standby odorant 2, the maximum and average GIA
- 495 concentrations within the enclosure are comparable between the hydrogen and methane tests. This also
- 496 confirms the hypotheses tested.
- 497 One important experimental design choice to consider is the use of volumetrically equivalent gas injection
- 498 rates, as opposed to energy injection rates. Indeed, due to the lower energy density of hydrogen at the
- 499 standard delivery pressure of domestic gas networks, the volumetric flow rate of hydrogen would be
- 500 about 3 times greater than that of natural gas to ensure an equivalent rate of energy delivery. However,
- 501 what our results have shown is that both hydrogen and methane escapes can be detected at equivalent
- 502 GIA concentrations and both at the required value of 1% GIA.
- 503

504 Table 3: Maximum and average gas in air concentrations within the enclosure at the point of first detection.

Gas in air saturation (ppm)	Test 4 Line Gas 10000 ppm	Test 17 Methane + NB 10000 ppm	Test 5 Hydrogen + NB 10000 ppm	Test 7 Hydrogen +NB 1000 ppm	Test 10 Hydrogen + Standby2 1000ppm	Test 18 Hydrogen + THT 10000 ppm
9000 - 10000						
8000 - 9000						
7000 - 8000						
6000 - 7000						
5000 - 6000						
4000 - 5000						
3000 - 4000						
2000 - 3000						
1000 - 2000						
0 - 1000						

505

Maximum ppm in the enclosure at the time of first detection Average ppm in the enclosure at the time of first detection

506 This study found that odorants appeared to remain with the hydrogen gas as it moves through an 507 enclosed space. Sprague and Flynn (2013) discussed that the molecular weight and dispersion properties 508 of hydrogen, relative to odorant compounds, were likely to lead to the odorant not remaining within the 509 gas stream in a stagnant environment (US 8 394 553 B2, 2013). However, they also suggested that in a 510 domestic dwelling, ventilation could be sufficient to drive dispersion and to keep the odorant mixed with 511 the gas stream (US 8 394 553 B2, 2013). The finding of this study supports this for hydrogen, natural gas 512 and methane.

513 One limitation of the study is the small number of participants in each test (3 to 4). The variation in

514 participant responses is apparent in a few tests. Detection occurred at 2000 ppm for test 17, whilst gas

515 concentration in tests 15 and 16 reached a maximum of 2500 ppm without the gas release being detected.

516 A similar observation can be made for test 12 were the escape was detected (but not identified as a gas

517 escape) at a lower concentration than the maximum measured in test 11, when no detection occurred in

test 11. This can be explained by the definition of "detection" used in this study to be when at least one

519 participant detected a smell. This increases the sensitivity of the results to the individual participant's

520 olfactory sensitivity. Despite these variations, if we compare our findings to previous olfactory testing

521 from Mouli-Castillo et al. (2020), which was performed on odorised hydrogen using standardised tests in

522 an accredited laboratory, we find that the odorant concentration in air from our work are within an order

- 523 of magnitude from those presented in that study. More specifically, our detection thresholds for
- 524 Hydrogen with New Blend, Standby Odorant 2 and THT, are 6.15, 4.5 and 2.2 times greater than the
- 525 ones from that study respectively. This can be explained, in part, by the use of 'naïve' participants in our

- 526 study, compared to an expert panel in their study. Another contributing factor is likely to be the fact that
- 527 our study mimic a real new dwelling environment with natural ventilation resulting in uneven
- 528 concentrations in the test volume, whereas olfactory measurements undertaken in their study are carried
- 529 out on precisely measured samples. It should also be noted that a variation of less than an order of
- 530 magnitude between olfactory studies with different methodologies should be considered a good match
- 531 (Murnane, Lehocky, & Owens, 2013). Both studies' conclusions agree that odorant in hydrogen will
- 532 induce an equivalent olfactory response to odorant in natural gas.

#### 533 Conclusion

- 534 This research is important because it addresses a key safety aspect of gas distribution: the odorisation of
- 535 gas to allow untrained people to detect gas escapes before they reach a flammable level. This research is
- 536 essential to the safety cases developed by hydrogen demonstration projects, in particular H100 in the UK
- 537 which aims to deliver 100% hydrogen to 300 homes via a purpose built distribution network.
- 538 By providing a direct comparison with methane, an approach which was not directly studied in the
- 539 standardised tests from Mouli-Castillo et al. (2020), it addresses the key requirement imposed by
- regulators in the UK that hydrogen distribution should be demonstrated to be 'as safe as' the currentnatural gas one.
- 542 Our work provides evidence that firstly, the odorants currently used within natural gas will have a similar
- 543 effectiveness in allowing escape detections when used with hydrogen. Secondly, that small escapes of
- 544 hydrogen are detectable in a comparable way to a natural gas escape in an equivalent room volume. These
- 545 conclusions can be considered robust as they were demonstrated by two different methodologies using
- 546 very different approaches.
- 547 These findings are also applicable to other innovation projects around the world which require the
- 548 demonstration that hydrogen can be effectively odorised and any releases detected. In particular, since the
- 549 odorant compounds tested are used in many countries.

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#### 685 Author Contributions

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#### 693 Competing Interest Statement

- 694 We certify that any and all of our affiliations with, or financial involvement with, any organization or
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