Project closure report
Hydrogen Odorant and Leak Detection Part 1, Hydrogen Odorant

October 2019

A consolidated summary report by Dr Arul Murugan, Senior Research Scientist (NPL)

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Document control

1. Introduction

1.1. Executive summary

This work programme was focused on identifying a suitable odorant for use in a 100% hydrogen gas grid (domestic use such as boilers and cookers). The research involved a review of existing odorants (used primarily for natural gas), and the selection of five suitable odorants based on available literature. One odorant was selected based on possible suitability with a Polymer Electrolyte Membrane (PEM) based fuel cell vehicle, which could in future be a possible end-user of grid hydrogen. NPL prepared Primary Reference Materials containing the five odorants in hydrogen at the relevant amount fraction levels (as would be found in the grid) including ones provided by Robinson Brothers (the supplier of odorants for natural gas in the UK). These mixtures were used by NPL to perform tests to understand the effects of the mixtures on pipeline (metal and plastic), appliances (a hydrogen boiler provided by Worcester Bosch) and PEM fuel cells. HSE investigated the health and environmental impact of these odorants in hydrogen. Olfactory testing was performed by Air Spectrum to characterise the 'smell' of each odorant. Finally, an economic analysis was performed by E4tech. The results confirm that Odorant NB would be a suitable odorant for use in a 100% hydrogen gas grid for combustion applications, but further research would be required if the intention is to supply grid hydrogen to stationery fuel cells or fuel cell vehicles. In this case, further testing would need to be performed to measure the extent of fuel cell degradation caused by the non-sulphur odorant obtained as part of this work programme, and also other UK projects such as the Hydrogen Grid to Vehicle (HG2V) project[1] would provide important information about whether a purification step would be required regardless of the odorant before the hydrogen purity would be suitable for a PEM fuel cell vehicle. If purification was required, it would be fine to use Odorant NB as this would be removed during the purification step.

1.2. Project background

The UK gas grid currently uses an odorant which allows citizens to quickly identify a gas leak. If the UK aims to decarbonise the gas grid by completely replacing natural gas with hydrogen, a robust assessment needs to be carried out to check whether the current odorant is still suitable for 100% hydrogen, or if not what the alternative should be. The objective of Part 1 of the SGN Hydrogen 100, Hydrogen Odorant and Leak Detection project was to trial five candidate hydrogen odorants and determine a suitable one for the future 100% hydrogen gas grid.

1.3. Supplier's background and qualifications

NPL's Energy Gases team is the sole provider of Primary Reference Materials for the UK's energy industries, and supplies gas standards to the natural gas, biomethane and hydrogen industry. This includes gas standards containing odorants in natural gas. NPL provides reference materials and calibration testing services under accreditation to ISO 17034 and ISO 17025, respectively, and is the UK's only laboratory that can perform quality assurance at hydrogen refuelling stations according to ISO 14687. NPL also sit on the key standardisation committees that develop ISO standards for the natural gas and hydrogen industries (as well as general gas analysis standards) including BSI PVE 3 8, BSI PTI 15, ISO TC 158, ISO TC 193 and ISO TC 197. Specifically, for this project, NPL have the capability to accurately prepare hydrogen mixtures containing odorants using their state-of-the-art gas mixtures preparation and analysis facilities.

1.4. Project objectives

The overall aim of the project was to identify, through a literature review, five potential odorants that would be suitable for a 100% hydrogen gas grid and carry out the necessary assessments to provide a final recommendation for the most suitable. The tasks that were carried out to achieve this selection were:

- Task 1.1: Criteria setting (NPL)
- Task 1.2: Identifying suitable odorant compounds (NPL)
- Task 1.3: Health/Environment (HSL)
- Task 1.4: Preparation of NPL Primary Reference Materials (NPL)
- Task 1.5: Olfactory testing (Air Spectrum)

- Task 1.6: Pipeline testing (NPL)
- Task 1.7: Flame boiler testing (NPL)
- Task 1.8: PEM fuel cell testing (NPL)
- Task 1.9: Economic analysis (E4Tech)
- Task 1.10: Odorant selection (NPL)

An overview of the selection process and key questions addressed are illustrated in Figure 1.
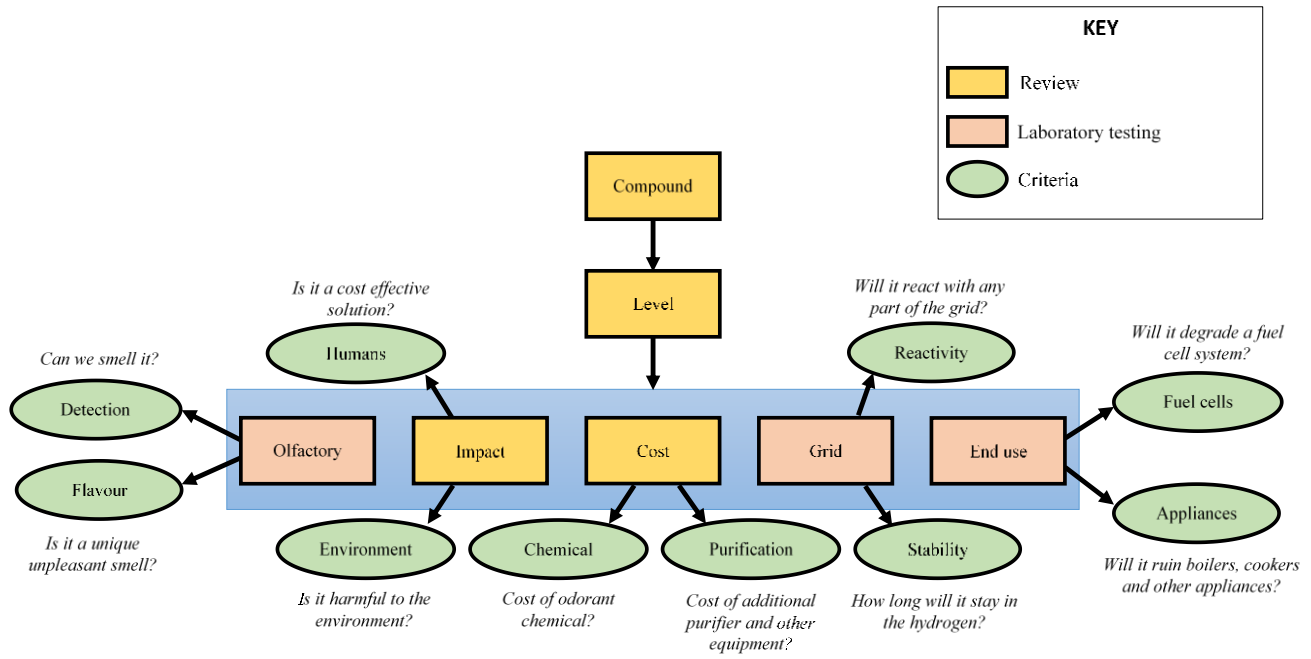
Figure 1: Overview of the activities

1.5.   Stakeholder engagement

The following stakeholders (i.e. outside of project consortium or subcontractors) were engaged during the project:

Who [Engage with]	What [Reason for engaging]	How [Method of communication]	When [Stage of project engagement occurred]
Robinson Brothers	**Sole supplier of odorants for the UK gas grids – they supplied odorants for this project**	**Email/phone/meeting**	**May 2018**
JD Pipes	**Provider of PE80 pipes – they provided samples of piping for this project**	**Email**	**October 2018**
JARI	**Trialled a hydrogen odorant in Japan**	**Meeting**	**May 2019**
Hy4Heat WP2	**Results of this project disseminated for development of Hy4Heat draft quality standard**	**Email**	**Jan 2019**

2. Project team structure

The project was led by Arul Murugan (Technical Lead) and Maria-Garcia Miranda (Project Lead) from NPL.

NPL science team:

Sam Bartlett/Robbie Wilmot/Arul Murugan (literature review/gas standard preparation) – Task 1.1, 1.2, 1.4 and 1.10

James Hesketh (pipeline and boiler testing) – Task 1.6 & 1.7

Luis Castanheira/Hans Becker (fuel cell testing) – Task 1.8

Paul Brewer/Thomas Bacquart/Fernando Castro/Gareth Hinds/Richard Brown (reviewers)

Subcontractors:

Air Spectrum (olfactory testing) – Task 1.5

E4Tech (economic analysis) – Task 1.9

HSL (health and environment assessment) – Task 1.3

Worcester Bosch (hydrogen boiler) – Task 1.7

3. Project delivery

The project commenced in April 2018 and comprised the following deliverables:

Deliverable	Outcome	Deadline (month)
D1.1	Process flow diagram – established criteria	M1
D1.2	Table – Candidate odorants and criteria assessment	M2
D1.3	Report – Assessment of impact	M3
D1.4	NPL PRMs – 10 gas mixtures of odorants in hydrogen	M6
D1.5	Report – Assessment of olfactory	M9
D1.6	Report – Assessment of end use performance	M9
D1.7	Report – Assessment of cost	M10
D1.8	Report – Final report with proposed odorant for hydrogen	M12

4. Conclusions

4.1.   Criteria setting

NPL wrote a report (shown in Appendix A) providing information on current odorants used in the UK such as Odorant NB and the relevant criteria that would be important when selecting an odorant for the 100% hydrogen gas grid. There is clear guidance around odour characteristics, physical properties and chemical properties for such an odorant.

For odour characteristic, ISO 13734 and IGEM/SR/16 recommends the odorant "exhibits a strong odour at very low concentrations and that the odour character is unpleasant, distinctive and not confusable with other frequently occurring odours at the network pressure of 7 bar(g) or less. This includes being able to distinguish the odour from that caused by the presence of any hydrogen sulphide and/or organic sulphur compounds present in the raw, untreated gas."

For physical properties it was identified that the odorant must remain homogeneous within the gas network, therefore a boiling point of higher than 130°C was recommended.

For chemical properties the main considerations were around purity of the odorant (where a purity of higher than 95% was recommended) and ensuring that the odorant remains stable within the gas (where an acceptable range was up to 8 hours).

Additionally, there exists gas quality guidance for hydrogen in the form of International Standard ISO 14687, where there is a technical specification for Grade A hydrogen for combustion applications such as boilers and cookers.

4.2.   Identifying suitable odorant compounds

As part of the report written for Appendix A, a review of all suitable odorants for gas was performed which identified 13 candidate compounds along with the relevant information regarding the criteria established in Section 4.1. Of the odorants identified, 8 were sulphur-based which would not be suitable for a fuel cell system (which would require hydrogen containing less than 4 nmol mol^{-1} of total sulphur). Two non-sulphur containing odorants were selected (GASODOR-S-FREE and 5-ethylidene-2-norbornene). Alongside these odorants, Odorant NB and Standby Odorant 2 were selected as they were the most commonly used odorants in the UK, as well as Odorant THT which the main odorant used across Europe. Therefore, the following five odorants were selected by NPL and SGN for this study and below provides rationale for the selection:

	Odorant name (including alternative names)	Compound	Rationale
1	Odorant NB, NB	78% 2-methyl-propanethiol, 22% dimethyl Sulphide	Primary odorant used by SGN and other UK gas networks
2	Standby Odorant 2, NB Dilute	34% Odorant NB, 64% Hexane	Diluted form of Odorant NB used by SGN if supply of Odorant NB is compromised
3	Odorant THT, THT	100% tetrahydrothiophene	Most commonly used odorant within European gas networks
4	GASODOR-S-FREE, Acrylates	37.4% ethyl acrylate, 60.1% methyl acrylate, 2.5% 2-ethyl-3methylpyrazine	Sulphur-free gas odorant in use within some German gas networks
5	5-ethylidene-2-norbornene, Norbornene	5-ethylidene-2-norbornene	Odorant with an unpleasant odour that is suitable for fuel cell applications

4.3.   Health/Environment

An assessment of the health and environment impacts of the five selected odorants, if released from a gas leak, was performed by HSL (Appendix B). Each odorant was assessed using guidance from the European Chemicals Agency.[2] The assessment concluded that all five odorants appeared to be fit-for-purpose with

regards to health and environment impact. However, it was highlighted that care should be taken when handling the compounds in pure form (for example on introduction to the gas grid).

4.4. Preparation of NPL Primary Reference Materials

To perform the tests as shown in Section 1.4, NPL produced Primary Reference Materials (PRMs) containing the five odorants (at levels that would be required in the gas grid) in hydrogen gas. PRMs provide a traceable link between high accuracy calibration gas standards and the SI definition of the mole; as such only National Metrology Institutes such as NPL can provide them. These mixtures must be prepared with the highest accuracies possible to ensure that any calibration gases produced by comparison to them are also accurate. To enable this, NPL prepare mixtures using gravimetric methods (i.e. each pure gas component is added individually, and the composition is calculated through accurate weighing of each addition).
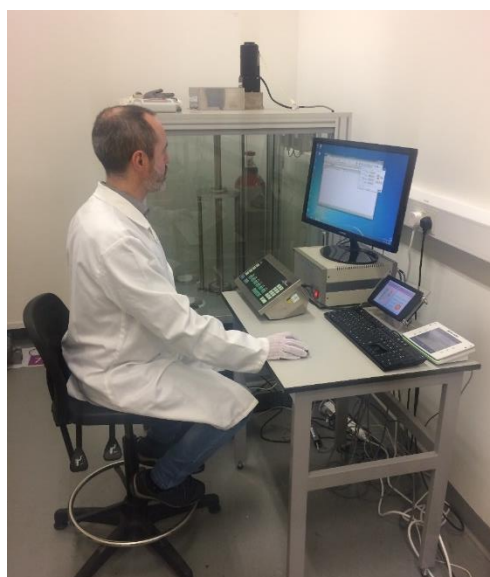
Figure 2: NPL scientist preparing a new PRM using high accuracy automated weighing facility

The PRMs prepared for this work are shown in the table below.

Cylinder number	Odorant name	Odorant compound	Amount fraction (μmol/mol)
Ng 812	Odorant NB	2-methyl-propanethiol	1.51
		Dimethyl Sulphide	0.43
NG 817	Standby odorant 2	Hexane	1.28
		2-methyl-propanethiol	0.51
		Dimethyl Sulphide	0.13
NG 846	Odorant THT	Tetrahydrothiophene	4.99
NG 815	GASODOR-S-FREE	Ethyl acrylate	1.12
		Methyl acrylate	0.70
		2-ethyl-3methylpyrazine	0.05
NG 845	5-ethylidene-2-norbornene	5-ethylidene-norbornene	17.0

Appendix C shows the output from the Gravcalc software[3] used by NPL to accurately determine gas compositions of the mixtures.

4.5.   Olfactory testing

NPL provided Air Spectrum with the five mixtures as shown in Section 4.4. They diluted the mixtures in air (by the same level for all mixtures) and subjected human participants to olfactory testing with the intention of assessing how suitable each odorant would be as a stenching agent for identifying a gas leak. Air Spectrum are UKAS accredited to BS EN 13725:2003, which was the service provided for this work and performed testing of all characteristics of the odorants as carried out in a standard olfactory testing for odorants in natural gas.

Figure 3: Olfactory testing with the five odorants in hydrogen mixtures performed at Air Spectrum

The suitability was based on odour concentration (how easily the odorant could be detected), the intensity (on the Sales scale) and character (whether it would distinguishable from other possible odours such as food). All odorants met the testing criteria for odour concentration and intensity. All odorants except 5-ethylidene-norbornene met the requirements for character testing, as they were perceived as unpleasant and gave smells that could be characterised as sulphur or oil. The 5-ethylidene norbornene was perceived as fruity (as well as sulphur and oil), which indicated that some customers would not immediately recognise a gas leak if this odorant was used in the gas grid. The entire report provided by Air Spectrum can be found in Appendix D.

4.6.   Pipeline testing

Two types of pipeline were sourced for testing; X42 carbon steel and PE80 polymer (Appendix E). The sources of material were cut into specimens that could be used to test for environment assisted cracking in different gas conditions (including under pressure). The PE80 polymer was tested at ambient pressure (to avoid measurement error associated with friction between the pull-rods and the seals) whereas the X42 carbon steel was tested at 7 barg to simulate gas network operating pressure. Tests were performed with specimens exposed to air, pure hydrogen and the five mixtures containing odorants in hydrogen. The overall conclusion was that the presence of any of the odorants in hydrogen made no difference to the results.

4.7. Flame boiler testing

NPL tested the effect of the five selected odorants on combustion through a hydrogen flame boiler (parts of a real hydrogen boiler were provided by Worcester Bosch for this test). The full report is provided in Appendix F. Hampton Thermodynamics performed a calculation to predict the chemistry of the condensate that would occur when the odorants underwent combustion, and solutions were made based on these predictions. The results indicated that the odorants containing no sulphur would not induce corrosion, whereas the sulphur-based odorants (which would provide a condensate containing sulphuric acid) were found to be more corrosive. However, these sulphur-based odorants in hydrogen appeared to be as corrosive as the current UK odorant in natural gas (used as the benchmark for these tests), indicating that there would be no issues with boiler compatibility.

4.8. PEM fuel cell testing

NPL performed fuel cell degradation testing using the five odorants in hydrogen mixtures produced as part of this project. Single cell PEM fuel cell was used for testing. To avoid any potential loss of sulphur within the system, all tubing and fittings were coated with Sulfinert treatment where possible. The cell voltage losses are shown below:
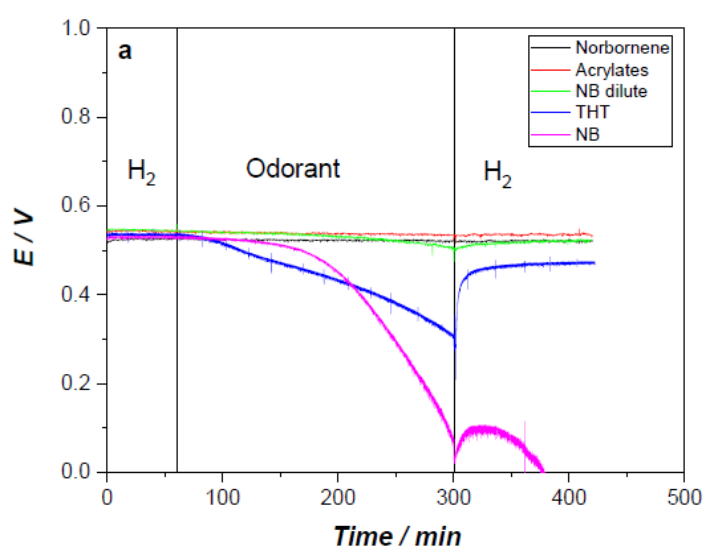
Identifier	Cell voltage loss after 4 h (mV)
Norbornene	5 ± 2
Acrylates	10 ± 2
NB dilute	40 ± 2
THT	225 ± 2
NB	460 ± 2

As shown in the results, and as expected from literature, the odorants containing sulphur caused noticeable degradation of the fuel cell. Whilst a loss of cell voltage was measured when subjecting the fuel cells to hydrogen containing the non-sulphur odorants (norbornene and acrylates), this voltage loss was significantly lower compared to the tests performed with sulphur odorants, and not dissimilar from the loss in voltage measured in the prior hydrogen purge step (from 0 – 60 minutes in the graph above) which used hydrogen BIP+. This indicates that further testing (including longer test duration tests and comparisons against pure hydrogen) would be required to conclude suitability of norbornene and acrylates. The results of these initial tests will be provided to the Cadent Gas HG2V project so that a further, long term fuel cell test can be performed with acrylates as part of the project. The full report from this work can be found in Appendix G.

4.9. Economic analysis

The technoeconomic report from E4Tech (Appendix H) concluded that if all odorants cause fuel cell degradation, the most cost-effective solution would be to continue using Odorant NB in a 100% hydrogen gas grid. This is based on the fact that Odorant NB is the lowest cost and because continuing to use Odorant NB would require minimal change to infrastructure and practice. In the scenario that hydrogen is supplied to stationery or transport fuel cells, the results of this work programme have indicated that a purification step may be required before hydrogen is supplied in case the odorant caused degradation of the fuel cell. However,

it was noted that if further extensive testing was carried out to prove that he acrylate odorant did not damage the fuel cell, and the price of this odorant was similar to NB odorant, it could become the preferable solution.

4.10. Odorant selection

	Odorant NB	Standby odorant 2	Odorant THT	GASODOR-S-FREE	5-ethylidene-2-norbornene
Health/environment	🟩	🟩	🟩	🟩	🟩
Olfactory	🟩	🟩	🟩	🟩	🟨
Pipeline	🟩	🟩	🟩	🟩	🟩
Flame boiler	🟩	🟩	🟩	🟩	🟩
Fuel cell	🟥	🟨	🟥	🟨	🟨
Economic	🟩	🟨	🟨	🟨	🟨

Based on the testing, review and analysis performed in this work programme, the conclusion is that for a 100% hydrogen gas grid used for heating (similar to the current natural gas grid), the current Odorant NB would remain the suitable odorant. This is because Odorant NB in hydrogen provides the characteristic gas leak smell and there were no indications of additional risk or damage to pipeline, appliances or residence (in comparison to natural gas). Economically, Odorant NB is the cheapest chemical and there would be no costs associated with changing current practice, suppliers or infrastructure (costs which may have been required when switching to another odorant). The results of this project do indicate that three of the odorants may be suitable for fuel cells (without a purification step), however further extensive tests would need to be carried out before it could be provided that any of the odorants would not damage a fuel cell. Other projects such as HG2V are investigating the feasibility of supplying grid hydrogen to vehicles, and one of the work packages is focused on understanding whether a purification step would be required. If purification was required, this step would remove the odorant as well, thus eliminating any requirement for an odorant suitable for fuel cells.

5. Recommendations

- Odorant NB is the recommended odorant for hydrogen in the gas grid as it meets the minimum requirements for odorants already used in natural gas.
- If the hydrogen gas grid is providing hydrogen to fuel cell vehicles/stationery fuel cells, further investigation would be required into whether a purification step would be required in order to purify grid hydrogen to meet ISO 14687 Grade D levels.
- If grid hydrogen is being provided to fuel cell vehicles/stationery fuel cells, and other research suggests that the odorant is the only impurity that would need to be removed to meet ISO 14687, further work should be carried out to extensively test fuel cell degradation, particularly using the non-sulphur odorants tested in this work programme.

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NPL REPORT CMES (RES) 037

SELECTION OF ODORANTS FOR A 100% HYDROGEN GRID

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NPLML - COMMERCIAL

MAY 2018

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CONTENTS

1   INTRODUCTION

The UK government is committed to reducing greenhouse gas emissions; by 2050 we must have reduced these emissions by 80% from the 1990 levels.[1] As highlighted in the UK's Clean Growth Strategy, the low carbon economy in the UK could grow by 11% between 2015 and 2030.[2] The UK gas infrastructure currently supplies natural gas to homes and industry; we are already reducing carbon emissions by introducing biomethane into the mix. With 90% of grid pipelines being replaced by polyethylene by 2032[3] and new technologies becoming available for efficient and renewable hydrogen production, a 100% hydrogen is certainly possible and would contribute significantly towards meeting the UK 2050 target. Before we can establish whether a scenario such as the 100% hydrogen grid would be possible, work is required to understand various implications, including safety.

Natural gas contains an odorant that can be detected via the human olfactory system at less than 20% of the gases lower flammability limit.[4] This established system quickly alerts any user to a leak of natural gas; it is simple but effective. Hydrogen is an odourless, hazardous material that has a wide flammability window ($4 - 74\%$) and can permeate through tiny leaks. Hydrogen production methods (commonly steam methane reforming or electrolysis) do not, as part of the process, introduce controlled amounts of odorant into the gas, and therefore an odorant would need to be added downstream. It is possible that current odorants used within the natural gas grid may be suitable in a 100% hydrogen grid, however extensive testing needs to be performed beforehand as, for example, the odorant may not behave the same way in hydrogen compared to natural gas. Other considerations are whether the odorant may affect new appliances, such as fuel cells, which require extremely pure hydrogen in order to operate efficiently. PEM (Polymer Electrolyte Membrane) fuel cells degrade extremely rapidly in the presence of hydrogen sulphide concentrations as low as 4 nmol mol^{-1} (ppb).[5]

This report provides the first outcome of the SGN funded Hydrogen 100: Hydrogen Odorants and Leak Detection project. In this report, a review of relevant standards and regulations has been performed in order to provide suitability criteria for an odorant that can be used within the UK's 100% hydrogen grid. Based on these criteria, a review of suitable odorants and their amount fraction levels has been provided with a recommendation of five potential candidates, as chosen by SGN.

Following the selection process, gas standards will be produced at NPL containing the five selected odorants in pressurised hydrogen. These standards will be used to perform experimental tests at the National Physical Laboratory (NPL) and Air Spectrum with support from Worcester Bosch and the Health and Safety Laboratory (HSL) as shown in Figure 1. Testing will include:
- Olfactory characterisation
- Fuel cell degradation
- Pipeline corrosion (both metal and plastic piping)
- Boiler corrosion
- Stability
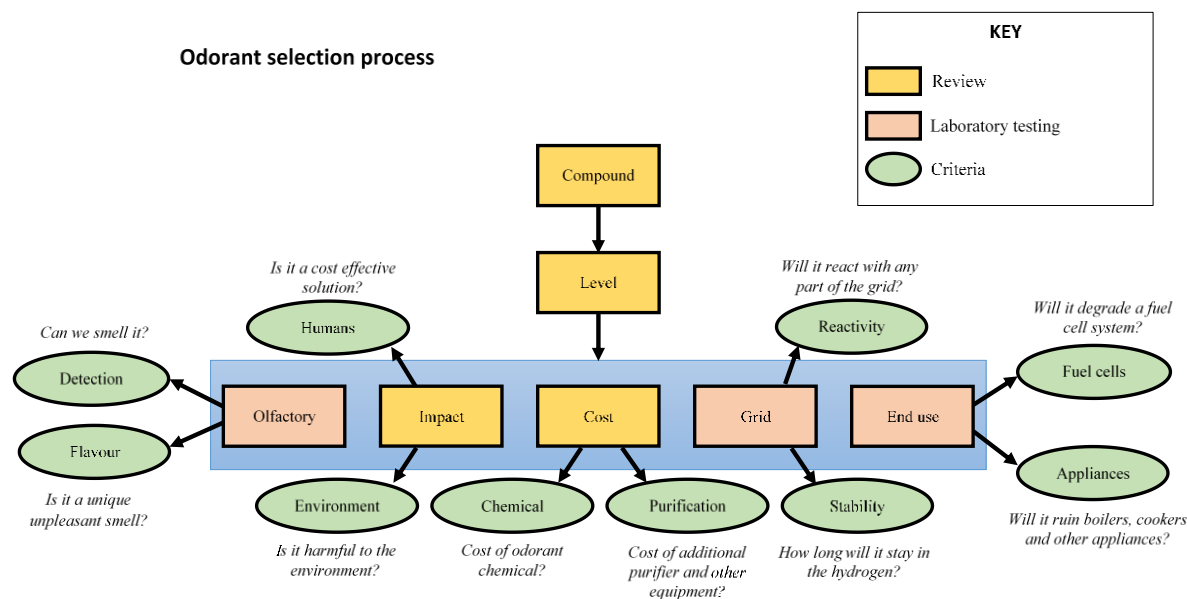- Health and environmental effects

Figure 1: Overview of selection process for a suitable odorant in the 100% hydrogen grid

2   CURRENT ODORANT IN THE NATURAL GAS GRID

Natural gas is an efficient, safe, colourless and odourless gas used as a source of energy for heating, cooking and electricity generation. Due to the lack of odour, an odorising compound is generally added to the natural gas as to make it detectable by the human olfactory system in the case of a leak. These compounds usually exhibit an unpleasant odour that is detectable at minute concentrations so as to act as a natural warning system in the event of a natural gas leak, prior to dangerous levels being reached.

Within the UK gas distribution network a two-part odorant known as Odorant NB (New Blend) is used, comprising of 78 % TBM (Tertiary butyl mercaptan) and 22 % DMS (Dimethyl sulphide) which gives the distributed gas its distinctive and recognisable "natural gas" odour. This is the principal odorant used within the UK and SGN, however other odorants and odorant combinations are also used in various circumstances, e.g. if the supply of Odorant NB is compromised or where gas throughput is very low. These include diluted odorants whereby Odorant NB is diluted with Hexane, e.g. 34 % Odorant NB and 66 % Hexane, Odorant THT (Tetrahydrothiophene) and Odorant EM (Ethyl mercaptan).

The odorant injection rate of Odorant NB into the grid requires control in order to achieve an odour intensity of 2.0° using the internationally agreed 'Sales Scale' at the point of gas usage. Currently within SGN this is equivalent to an injection rate of 6 mg m^{-3} resulting in an odorant concentration of approximately 1.3 µmol mol^{-1} TBM and 0.5 µmol mol^{-1} DMS within the odorised natural gas. At this intensity, gas leaks and escapes should be readily detectable by the human olfactory system at a concentration of gas in air not exceeding 1 % and is therefore sufficient to meet the requirements of the GS(M)R Schedule 3 part 1.[6]

The injection of Odorant NB into the grid at 6 mg m^{-3} is standard practice within the UK in order to meet requirements of technical standards and regulations. Practices across Europe however are varied both in terms of the odorants used and the regulatory requirements needed to be met. Odorant THT is the most widely used odorant across Europe, however other odorants are also used in varying combinations. Other odorants include IPM (iso propyl mercaptan), NPM (Propyl mercaptan), MES (Methyl ethyl sulphide) and sulphur-free odorants. Sulphur-free odorants, such as GASODOR-S-FREE (37.4% MA (Methyl acrylate), 60.1% EA (Ethyl acrylate), and 2.5% EMP (2-ethyl-3-methylpyrazine)) are seeing increased usage, particularly in Germany, the distribution network of which is regulated by DVGW standard G280-1.[7]

3   ESTABLISHING CRITERIA

In order to select suitable odorants for a 100% hydrogen grid, selection criteria must be well established. In this section, criteria have been selected based around odour characteristics, physical properties, chemical properties and quality (e.g. expected effects to appliances or gas systems). These criteria are based upon existing standards for natural gas odorisation which would most likely apply for hydrogen odorisation. Additionally, it should be noted that quality standards for hydrogen appliances and fuel cell applications have already been written by ISO TC 197 and these specifications are important during the selection process of a suitable hydrogen odorant.

3.1 ODOUR CHARACTERISTICS

Published standards and regulations such as ISO 13734[4] and IGEM/SR/16 Edition 2[8] provide guidance and recommendations regarding the characteristics of suitable odorant compounds used within the gas grid. In summary, it is recommended that a suitable odorant exhibits a strong odour at very low concentrations and that the odour character is unpleasant, distinctive and not confusable with other frequently occurring odours at the network pressure of 7 bar(g) or less. This includes being able to distinguish the odour from that caused by the presence of any hydrogen sulphide and/or organic sulphur compounds present in the raw, untreated gas. At an appropriate injection rate, the odorised gas should exhibit an odour intensity of 2.0° on the Sales Scale at a concentration of 20% of the lower flammability limit (LFL) with the odour character remaining the same at varying dilutions of gas in air.

3.2 PHYSICAL PROPERTIES

The physical properties of suitable odorant compounds must be such that they remain homogenous within the distributed gas network under standard operating and storage conditions. The volatility of the odorant is the most important property and should be high enough as to not appreciably condense under existing pipeline conditions. It is therefore recommended that the boiling point of odorant components be less than 130°C. Odorant components should not leave appreciable residues after evaporation (< 0.2%) and/or leave significant solid deposits after combustion. It is also recommended that less than 2% by volume of odorant be soluble in water and that the odorant is usable at low temperatures. The main reason it is not recommended to use TBM as a single component odorant is due to its high freezing point, meaning it would not be sufficiently vaporised at low temperatures and thus not detected.

3.3 CHEMICAL PROPERTIES

How an odorant behaves chemically when mixed with the gas distribution network is of high importance to ensure both the quality of the gas at point of use and the safety of end users. The odorant used must be of sufficient purity as to not introduce significant impurity levels into the distributed gas. Currently it is recommended that the odorant be ≥ 95% pure. In order to ensure the safety of gas distributers and end users it is imperative that the odorant remains stable within the network, with grid gas retaining an odour within an acceptable range for up to 8 hours following cessation of odorant injection. It is also critical that the resulting odorised gas is not harmful or toxic. Sulphur-free odorants, such as GASODOR-S-FREE, are odorants composed primarily of acrylate compounds. Acrylate-based non-sulphur odorants have a tendency to polymerise under standard grid operating conditions, therefore a stabilising compound (2-ethyl-3-methylpyrazine in GASODOR-S-FREE) is required to prevent this.

3.4 GAS QUALITY

3.4.1   GS(M)R 1996

The Gas Safety (Management) Regulations 1996 provide guidance for natural gas distributed within the UK. The regulations provide quality specifications for the content and characteristics of natural gas as shown in Figure 2.

Content or characteristic	Value
hydrogen sulphide content	≤5mg/m³;
total sulphur content (including H_2S)	≤50mg/m³;
hydrogen content	≤0.1% (molar);
oxygen content	≤0.2% (molar);
impurities	shall not contain solid or liquid material which may interfere with the integrity or operation of pipes or any gas appliance (within the meaning of regulation 2(1) of the 1994 Regulations) which a consumer could reasonably be expected to operate;
hydrocarbon dewpoint and water interfere dewpoint	shall be at such levels that they do not with the integrity or operation of pipes or any gas appliance (within the meaning of regulation 2(1) or the 1994 Regulations) which a consumer could reasonably be expected to operate;
WN	(i) ≤51.41 MJ/m³, and (ii) ≥47.20 MJ/m³;
ICF	≤0.48
SI	≤0.60

Figure 2: Content and characteristics of natural gas from GS(M)R 1996

These specifications provide an upper limit for hydrogen sulphide at 5 mg m^{-3} and for total sulphur content at 50 mg m^{-3} which would influence the selection process for a suitable odorant. It is assumed that these limits would also be applicable to a 100% hydrogen grid, however as discussed further in Section 3.4, other new quality standards which are directly related to hydrogen (rather than natural gas) may provide more suitable quality requirements for this study.

3.4.2   ISO 14687-1:1999[9]

ISO 14687-1 provides guidance on three quality grades of hydrogen for different applications:
-    Grade A: Boilers and cookers
-    Grade B: Heat and power
-    Grade C: Aircraft and space vehicles

There are further grades for liquid hydrogen which will not be reviewed as part of this study. The quality requirements for hydrogen gas in ISO 14687-1 is shown in Figure 3.

Constituents	Type I		
(assay)	Grade A	Grade B	Grade C
Hydrogen fuel index [a] (minimum mole fraction, %)	98,0 %	99,90 %	99,995 %
Para-hydrogen (minimum mole fraction, %)	NS	NS	NS
Impurities (maximum content)			
Total gases	20.000 µmol/mol	1.000 µmol/mol	50 µmol/mol
Water (mole fraction, %)	Non-condensing at all ambient conditions [b]	Non-condensing at all ambient conditions	c
Total hydrocarbon	100 µmol/mol	Non-condensing at all ambient conditions	c
Oxygen	b	100 µmol/mol	d
Argon	b		d
Nitrogen	b	400 µmol/mol	c
Helium			39 µmol/mol
CO_2			e
CO	1 µmol/mol		e
Mercury		0,004 µmol/mol	
Sulfur	2,0 µmol/mol	10 µmol/mol	
Permanent particulates	g	f	f
Density			

[a] The hydrogen fuel index is determined by subtracting the "total non-hydrogen gases" expressed in mole percent, from 100 mole percent.

[b] Combined water, oxygen, nitrogen and argon: maximum mole fraction of 1,9 %.

[c] Combined nitrogen, water and hydrocarbon: max. 9 µmol/mol.

[d] Combined oxygen and argon: max. 1 µmol/mol.

[e] Total CO_2 and CO: max. 1 µmol/mol.

[f] To be agreed between supplier and customer.

[g] The hydrogen shall not contain dust, sand, dirt, gums, oils, or other substances in an amount sufficient to damage the fuelling station equipment or the vehicle (engine) being fuelled.

Figure 3: Quality specifications for hydrogen gas applications as shown in ISO 14687-1

ISO 14687-1 recommends a maximum threshold limit of 2 µmol mol^{-1} of total sulphur and 100 µmol mol^{-1} of total hydrocarbons in hydrogen used for hydrogen boilers and cookers. It should be noted however that this standard was written in 1999 and may not have consulted the relevant experts who could advise the suitable threshold limits for hydrogen boilers and cookers. Therefore, whilst ISO 14687-1 can be used as a guide, direct consultation with manufacturers of these types of appliances would be preferable.

3.4.3   ISO 14687-2:2015[5]

ISO 14687-2 provides guidance on the purity specifications for hydrogen used in PEM fuel cells for hydrogen vehicles. This standard provides very low threshold limits for 13 gaseous impurities in hydrogen as shown in Figure 4.

Characteristics (assay)	Type I, Type II
	Grade D
Hydrogen fuel index (minimum mole fraction)[a]	99,97 %
Total non-hydrogen gases	300 μmol/mol
Maximum concentration of individual contaminants	
Water (H_2O)	5 μmol/mol
Total hydrocarbons[b] (Methane basis)	2 μmol/mol
Oxygen (O_2)	5 μmol/mol
Helium (He)	300 μmol/mol
Total Nitrogen (N_2) and Argon (Ar)[b]	100 μmol/mol
Carbon dioxide (CO_2)	2 μmol/mol
Carbon monoxide (CO)	0,2 μmol/mol
Total sulfur compounds[c] (H_2S basis)	0,004 μmol/mol
Formaldehyde (HCHO)	0,01 μmol/mol
Formic acid (HCOOH)	0,2 μmol/mol
Ammonia (NH_3)	0,1 μmol/mol
Total halogenated compounds[d] (Halogenate ion basis)	0,05 μmol/mol
Maximum particulates concentration	1 mg/kg

For the constituents that are additive, such as total hydrocarbons and total sulfur compounds, the sum of the constituents are to be less than or equal to the acceptable limit.

[a] The hydrogen fuel index is determined by subtracting the "total non-hydrogen gases" in this table, expressed in mole percent, from 100 mole percent.

[b] Total hydrocarbons include oxygenated organic species. Total hydrocarbons shall be measured on a carbon basis (μmolC/mol). Total hydrocarbons may exceed 2 μmol/mol due only to the presence of methane, in which case the summation of methane, nitrogen and argon shall not exceed 100 μmol/mol.

[c] As a minimum, total sulphur compounds include H_2S, COS, CS_2 and mercaptans, which are typically found in natural gas.

[d] Total halogenated compounds include, for example, hydrogen bromide (HBr), hydrogen chloride (HCl), chlorine (Cl2), and organic halides (R-X).

Figure 4: Quality specifications for hydrogen fuel cell vehicles as shown in ISO 14687-2

As shown, the concentration of total sulphur compounds in hydrogen used with fuel cell vehicles must be below 4 nmol mol^{-1} whereas odorants commonly used in natural gas would be present at much higher levels in the μmol mol^{-1} range. Unless the odorant is sulphur-free odorant and can be shown not to cause degradation of a fuel cell, an additional purification step would be required to remove the odorant before the hydrogen can be provided to the vehicle. This would incorporate an additional cost due to the purification step. The alternative solution is to not consider fuel cell vehicle applications as part of the 100% hydrogen grid plan.

3.4.4   ISO 14687-3:2014[10]

ISO 14687-3 provides guidance on the purity specifications for hydrogen used in stationary fuel cells. This standard provides very low threshold limits for total sulphur compounds as shown in Figure 5.

Characteristics[a] (assay)	Type I, grade E		
	Category 1	Category 2	Category 3
Hydrogen fuel index (minimum mole fraction)	50 %	50 %	99,9 %
Total non-hydrogen gases (maximum mole fraction)	50 %	50 %	0,1 %
Water (H_2O)[b]	Non-condensing at all ambient conditions	Non-condensing at all ambient conditions	Non-condensing at all ambient conditions
Maximum concentration of individual contaminants			
Total hydrocarbons (C_1 basis)[c]	10 µmol/mol	2 µmol/mol	2 µmol/mol
Oxygen (O_2)	200 µmol/mol	200 µmol/mol	50 µmol/mol
Nitrogen (N_2), Argon (Ar), Helium (He) (mole fraction)	50 %	50 %	0,1 %
Carbon dioxide (CO_2)	Included in total non-hydrogen gases	Included in total non-hydrogen gases	2 µmol/mol
Carbon monoxide (CO)	10 µmol/mol	10 µmol/mol	0,2 µmol/mol
Total sulfur compounds[d]	0,004 µmol/mol	0,004 µmol/mol	0,004 µmol/mol
Formaldehyde (HCHO)	3,0 µmol/mol	0,01 µmol/mol	0,01 µmol/mol
Formic acid (HCOOH)	10 µmol/mol	0,2 µmol/mol	0,2 µmol/mol
Ammonia (NH_3)	0,1 µmol/mol	0,1 µmol/mol	0,1 µmol/mol
Total halogenated compounds[e]	0,05 µmol/mol	0,05 µmol/mol	0,05 µmol/mol
Maximum particulates concentration	1 mg/kg	1 mg/kg	1 mg/kg
Maximum particle diameter	75 µm	75 µm	75 µm

Figure 5: Quality specifications for hydrogen stationary fuel cells as shown in ISO 14687-3

As with fuel cell vehicle applications, conventional odorants would not be suitable for use with stationary fuel cell appliances, therefore if hydrogen were to contain these types of compounds, then a costly purification step would be required.

4   SELECTION OF SUITABLE ODORANTS

4.1 REVIEW OF CANDIDATE ODORANTS

This section provides a literature review of potential candidate odorants for a 100% hydrogen grid as found in existing international standards, peer-reviewed papers and patents. For each odorant identified, relevant information is provided which will help to determine how suitable the odorant would be in accordance to the criteria set in Section 3. The identified odorants as shown in Table 1 along with relevant information (where information was not available a blank is shown).

Table 1: Review of candidate odorants for the 100% hydrogen grid

Odorant	Amount		Olfactory		Impact		Cost		Grid		End use		Physical Properties			Chemical Properties		Meeting Technical Specifications		NMI Capability		Reference
	Injection rate (mg/m3)	Amount fraction in natural gas	Strength	Flavour	Health	Environment	Chemical	Purification	Reactivity	Stability	Fuel cells	Appliances	Residue/Deposit	Boiling point	Vapour pressure	Toxicity	Solubility in water	GSMR 1996	EN 16726	Preparation	Measurement	
Odorant NB (78% TBM, 22% DMS)	6	1.27 ppm TBM, 0.52 ppm DMS	2 Sales Scale	Recognised in UK as smell of natural gas	Harmful / Irritant	Toxic to aquatic organisms + Flammable	CONTACTING ROBINSON BROS		Stable	Over 8 hours in grid	Not suitable	Suitable	No	55°C		Non-toxic	Insoluble	Suitable	Suitable	Yes	Yes	SGN-PM-GQ-2[11]
Standby odorant (8% Odorant NB, 92% Hexane)			2 Sales Scale	Unpleasant	Health Hazard	Toxic to aquatic organisms + Flammable	CONTACTING ROBINSON BROS		Stable	Over 8 hours in grid	Not suitable	Suitable	No	>55°C	160 mbar	Toxic	Insoluble	Suitable	Suitable	Yes	Yes	SGN-PM-GQ-2
Standby odorant 2 (34% Odorant NB, 66% Hexane)			2 Sales Scale	Unpleasant	Health Hazard	Toxic to aquatic organisms + Flammable	CONTACTING ROBINSON BROS		Stable	Over 8 hours in grid	Not suitable	Suitable	No	>55°C		Toxic	Insoluble	Suitable	Suitable	Yes	Yes	SGN-PM-GQ-2
Odorant THT (100% THT)	18	5 ppm	2 Sales Scale	Stench	Harmful / Irritant	Toxic to aquatic organisms + Flammable	CONTACTING ROBINSON BROS		Stable	Over 8 hours in grid	Not suitable	Not suitable	No	119°C	24 mbar	Non-toxic	Insoluble	Suitable	Suitable	Yes	Yes	SGN-PM-GQ-2
Gasodor S-Free (37.4% methly acrylate + 60.1% ethyl acrylate + 2.5% 2-ethyl-3-methylpyrazine)	8	0.85 ppm MA, 1.17 ppm EA, 0.04 ppm 2E3MP	Level 3 of Intensity	Characteristic	Harmful / Irritant	Toxic to aquatic organisms + Flammable	CONTACTING SYMRISE		Stable		Claims to be suitable	Suitable	No	80°C	83 mbar	Toxic	Insoluble	Suitable	Suitable	Yes	Yes	EN 16726[12]
TBM (79%) + IPM (15%) + NPM (6%)	6	1.28 ppm TBM, 0.29 ppm IPM, 0.12 ppm NPM							Stable		Not suitable	Suitable		62°C				Suitable	Suitable	Yes	Yes	EN 16726
THT (85%) + TBM (15%)	16	3.77 ppm THT, 0.65 ppm TBM							Stable		Not suitable	Suitable		65°C				Suitable	Suitable	Yes	Yes	EN 16726
EM	8	3.15 ppm		Skunk	Harmful / Irritant	Toxic to aquatic organisms + Flammable			Stable		Not suitable	Not suitable	No	35°C	589 mbar	Non-toxic	Insoluble	Suitable	Suitable	Yes	Yes	EN 16726
DES	12	3.3 ppm		Garlic	Harmful / Irritant	Flammable					Not suitable	Not suitable	No	92°C	80 mbar	Non-toxic	Insoluble	Suitable	Suitable	Yes	Yes	Exploration of H2 odorants[13]
2,3-butanedione	16	5 ppm		Putrid Butter	Corrosive	Flammable					Suitable	Not tested		88°C	76 mbar	Toxic	Soluble			No	No	Exploration of H2 odorants
Ethyl sugar lactone	0.00052	0.0001 ppm		Caramel	Non-hazardous	Non-hazardous					Suitable	Not tested		184°C		Non-toxic	No data available			No	No	Exploration of H2 odorants
Ethyl isobutyrate	11	2.2 ppm		Fruity	Non-hazardous	Flammable					Suitable	Not tested		112°C	53	Non-toxic	No data available			No	No	Exploration of H2 odorants
5-ethylidene-2-norbornene	84	17 ppm		Coal gas	Health Hazard	Toxic to aquatic organisms + Flammable					Suitable	Not tested		146°C	5.6	Toxic	Insoluble			No	No	Exploration of H2 odorants

4.2 REVIEW OF CANDIDATE ODORANTS

As shown in Table 1, there are thirteen odorants identified in the literature; eight of these odorants are sulphur-based odorants that are used within the UK and Europe for natural gas odorisation, however some non-sulphur odorants have also been identified, some of which may be suitable for hydrogen to be used in fuel cell applications. As advised by SGN, Odorant NB will be selected for further study as it is the primary odorant used within the UK gas distribution network. NPL advises that at least one of the five odorants selected for further testing is one that may be suitable for fuel cell applications, as it is possible that the future 100% hydrogen grid may be adapted for supplying hydrogen at 700 bar to refuelling stations.

4.3 FINAL SELECTION OF CANDIDATE ODORANTS

From the odorant candidates identified in Table 1, five have been selected for further assessment and testing within the scope of this project (Tasks 1.3 – 1.9) and are shown in Table 2 along with the rationales. These five odorants were selected by NPL and SGN on the basis that they are currently used to odorise gas networks within Europe or are odorants that are suitable for fuel cell applications. Additionally, the five odorants below were selected as they all have unpleasant and recognisable odours.

Table 2: The five selected odorant compounds

	Compound	Rationale
1	Odorant NB (78% TBM), 22% DMS)	Primary odorant used by SGN and other UK gas networks
2	Standby Odorant 2 (34% Odorant NB, 66% Hexane)	Diluted form of Odorant NB used by SGN if supply of Odorant NB is compromised
3	Odorant THT (100% THT)	Most commonly used odorant within European gas networks
4	GASODOR-S-FREE (37.4% MA, 60.1% EA, 2.5% EMP)	Sulphur-free gas odorant in use within some German gas networks
5	5-ethylidene-2-norbornene	Odorant with an unpleasant odour that is suitable for fuel cell applications

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APPENDIX B

HEALTH & SAFETY LABORATORY

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HMX/18/18

HEALTH & SAFETY LABORATORY

Technical Comment on Odorants Shortlisted by NPL for a 100% Hydrogen Grid

Date of Issue:	July 2018
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Project number:	PE03583

Disclaimer:

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CONTENTS

1   INTRODUCTION

This document describes the outcomes of the work described within the HSL proposal entitled "Human and Environmental Impact Assessment of Odorants" prepared for the Health and Safety Laboratory (HSL) for NPL on 11th April 2018. More specifically, this document provides an evaluation of the health and environmental impact of each of 5 different gas odorants shortlisted by NPL.

Shortlisted odorants are: Odorant NB

                                                Standby odorant 2

                                                Tetrahydrothiophene (THT)

                                                Gasodor-S-free

                                                5-Ethylidene-2-norbornene

Each odorant will be considered in turn over the following sections, key information on physical properties, synonyms, health effects and environmental effects will be considered.   Where appropriate, each odorant compound has been an assessed using the principles outlined in the CLP guidance for toxicity estimation [1] – Note: CLP Guidance is the general term given to the publication of the European Chemicals Agency (ECHA) to assist users in complying with the correct classification, labelling and packaging (CLP) for individual chemical substances (and mixtures).

2   ODORANT NB

2.1   APPEARANCE / PHYSICAL PROPERTIES OF INDIVIDUAL COMPONENTS OF ODORANT NB

Odorant NB is a mixture consisting of 2 discrete chemical compounds: 2-methyl-2-propanethiol (78%) and methyl sulphide (22%).

2.1.1   2-Methyl-2-propanethiol

2-Methyl-2-propanethiol has an unpleasant, 'strong offensive' [2] or 'heavy skunk' [3] odour. It is a colourless liquid with a boiling point of 64°C [4].

In terms of solubility, it is described as being slightly soluble in water and very soluble in alcohol, ether and liquid hydrogen sulphide [2]. As a liquid 2-methyl-2-propanethiol is less dense than water (density: 0.79 g/cm^3, water is 1.0 g/cm^3), as a gas it has a much higher relative vapour density to air (vapour density 3.1 (air = 1)) [4]. 2-Methyl-2-propanethiol is classified as flammable, although no flammable limit values are reported, it has a flash point of <-29°C [5].

The SDS for 2-methyl-2-propanethiol carries the following United Nations Globally Harmonised System of Classification of Labelling of Chemicals (GHS) pictograms and hazard statements:

H225   Highly flammable liquid and vapour

H317   May cause and allergic skin reaction

H411   Toxic to aquatic life with long lasting effects

2.1.2   Methyl Sulphide

Methyl sulphide (sometimes known as dimethyl sulphide) has an unpleasant, 'cabbage like' [6] odour. It is a colourless liquid with a boiling point of 37°C [7]

In terms of solubility, it is described as being slightly soluble in water and soluble in ethanol and ethyl ether [7]. As a liquid (methyl sulphide) is less dense than water (density: 0.85 g/cm^3, water is 1.0 g/cm^3)[7], as a gas it has a higher relative vapour density to air (vapour density 2.1 (air = 1)) [8]. Methyl sulphide is flammable, the lower flammability limit (LFL) is 2.2% v/v in air and the upper limit (UFL) is 19.7% v/v [9], it has a flash point of -48°C [10].

Safety Data Sheet (SDS) for methyl sulphide carries the following GHS pictograms and hazard statements:

H225   Highly flammable liquid and vapour

H319   Causes serious eye irritation

2.2   SYNONYMS OF INDIVIDUAL COMPONENT GASES OF ODORANT NB

2.2.1   Synonyms of 2-Methyl-2-propanethiol
tert-Butyl mercaptan
tert-Butylthiol
tert-Butanethiol
2-Methylpropane-2-thiol
TBM
[75-66-1] CAS Number

2.2.2   Synonyms of Methyl Sulphide
Dimethyl sulphide
Methylsulfide
Dimethyl sulfide
Methyl monosulfide
Dimethyl monosulfide
[75-18-3] CAS Number

2.3   HEALTH EFFECTS OF INDIVIDUAL COMPONENT GASES OF ODORANT NB
Both 2-methyl-2-propanethiol (LD_{50} (oral-rat) 4729 mg/kg)[11]and methyl sulphide (LD_{50} (oral-rat) 3300 mg/kg)[12] have LD_{50} (oral) values in excess of 2000 mg/kg. CLP guidance (section 1.6.4.1 of reference 1) states that components of mixtures with LD_{50} values > 2000 mg/kg are excluded from toxicity classification. Note: LD_{50} is the median lethal dose or 'lethal dose, 50%' which expresses in mg/kg the quantity of a substance required to be administered to kill 50% of the test sample.

2.4   ENVIRONMENTAL EFFECTS OF INDIVIDUAL COMPONENT GASES OF ODORANT NB

Only 2-methyl-2-propanethiol carries a specific environmental hazard phrase (H411-Toxic to aquatic life with long lasting effects). However, due to the fact that the component will only be present in a very dilute concentration (1.3 µmol/mol) within the bulk gas stream, any impact on the environment arising from 2-methyl-2-propanethiol can largely be discounted.

3   STANDBY ODORANT 2

3.1   INDIVIDUAL COMPONENTS OF STANDBY ODORANT 2
Standby odorant 2 is made up of odorant NB (34%), diluted within a hexane solution (66%). As a result, the summary for individual components of odorant NB (Sections 2.1.1-2.4) applies. The information for hexane has been based on n-hexane (hexane exists as a range of different chemical isomers, molecules with the same chemical formula but in different structural arrangements, with broadly similar physical characteristics).

3.2   APPEARANCE / PHYSICAL PROPERTIES OF HEXANE
Hexane has a 'gasoline-like' [13] odour. It is a colourless liquid with a boiling point of 69°C [14].

In terms of solubility, it is described as barely soluble in water (9.5 mg/l)[15], very soluble in ethanol and very soluble in ethyl ether and chloroform [16]. As a liquid hexane is significantly less dense

than water (density: 0.66 g/cm^3, water is 1.0 g/cm^3)[16], as a gas it has a higher relative vapour density to air (vapour density 2.97 (air = 1)) [17]. Hexane is flammable, the lower flammability limit (LFL) is 1.2% v/v in air and the upper limit (UFL) is 7.5% v/v [18], it has a flash point of -22°C [19].

Safety Data Sheet (SDS) for hexane carries the following GHS pictograms and hazard statements:

H225   Highly flammable liquid and vapour

H304   May be fatal is swallowed and enters airways

H315   Causes skin irritation

H319   Causes serious eye irritation

H336   May cause drowsiness or dizziness

H361f   Suspected of damaging fertility

H373   May cause damage to organs through prolonged or repeated exposure

H411   Toxic to aquatic life with long lasting effects

3.3 SYNONYMS OF HEXANE

Although most generally known as hexane, it can also be known as:

Hexanes
n-Hexane
[92112-69-1] (CAS Number)

3.4 HEALTH EFFECTS OF HEXANE

Hexane has an oral LD_{50} (oral-rat) of 15840 mg/kg)[20], placing it well above the CLP exemption limit of 2000 mg/kg for acute toxicity estimation. However, it is clear that health effects must be considered at the point of introduction of odorant to the gas, where the odorant is present in its concentrated form. It is of note that hexane has workplace exposure limits (Table 1) [21].

Table 1; Workplace Exposure Limits for Hexane (taken from HSE EH-40/2005)

Substance	CAS Number	Workplace Exposure Limit			
		Long-term exposure limit (8-hr TWA reference period)		Short-term exposure limit (15 minute reference period)	
		ppm	mg.m^{-3}	ppm	mg.m^{-3}
n-Hexane	[110-54-3]	20	72	---	---

3.5   ENVIRONMENTAL EFFECTS OF HEXANE

Hexane carried a specific environmental hazard phrase (H411-Toxic to aquatic life with long lasting effects). However, due to the fact that the component will only be present in a very dilute concentration within the bulk gas stream, any impact on the environment arising from hexane can largely be discounted.

4   TETRAHYDROTHIOPHENE

4.1   APPEARANCE / PHYSICAL PROPERTIES OF TETRAHYDROTHIOPHENE

Tetrahydrothiophene (THT) is colourless liquid with a boiling point of 119-121°C [22]. It is reported to have a distinct 'stench' [23], with an odour threshold of 1 part per billion [24].

In terms of solubility, tetrahydrothiophene is insoluble in water, but fully miscible in all proportions in alcohol, ether, acetone, benzene and other organic solvents [25]. As a liquid, tetrahydrothiophene is very slightly less dense than water (density: 0.9987 g/cm^3 [25], water is 1.0 g/cm^3), as a vapour it has a relative vapour density significantly greater than air (vapour density 3.05 (air = 1)) [22]. Tetrahydrothiophene is flammable, with a flash point of 13°C [23]. However, no flammable range data has been reported.

SDS for tetrahydrothiophene carries the following GHS pictograms and hazard statements:

H225   Highly flammable liquid and vapour

H302   Harmful if swallowed

H312   Harmful in contact with skin

H315   Causes skin irritation

H319   Causes serious eye irritation

H332   Harmful if inhaled

H412   Harmful to aquatic life with long lasting effects

4.2   SYNONYMS OF TETRAHYDROTHIOPHENE

Although most generally known as tetrahydrothiophene, it can also be known as:

Thiolane
Thiophane
Thiacyclopentane
Tetramethylene sulfide

Tetramethylene sulphide

[110-01-0] (CAS Number)

4.3   HEALTH EFFECTS OF TETRAHYDROTHIOPHENE

Tetrahydrothiophene has an oral LD_{50} (oral-rat) of 1750 mg/kg)[14]. This value has been used to feed into the required CLP calculation for the mixture (Appendix A). Although health effects must be considered at the point of introduction of odorant to the gas, where the odorant is present in its concentrated form, once diluted by the bulk gas, its health effects can be discounted.

4.4   ENVIRONMENTAL EFFECTS OF TETRAHYDROTHIOPHENE

Tetrahydrothiophene carries a specific environmental hazard phrase (H412-Harmful to aquatic life with long lasting effects). In common with the health effects, the environmental impact is present at point of introduction where the odorant is present in concentrated form. Once diluted by the bulk gas, its environmental effects can be discounted.

5   GASODOR-S-FREE

5.1   APPEARANCE / PHYSICAL PROPERTIES OF INDIVIDUAL COMPONENTS OF GASODOR-S-FREE

Gasodor-S-free is a mixture consisting of 3 discrete chemical compounds: methyl acrylate (37.4%), ethyl acrylate (60.1%) and 2-ethyl-3-methylpyrazine (2.5%).

5.1.1   Methyl Acrylate

Methyl acrylate has a distinctive acrid odour, with a reported odour threshold of ca. 20ppm [26]. It is a colourless liquid with a boiling point of 80.5°C [27]

In terms of solubility, it is described as being slightly soluble in water (6 g/100 ml) [27] and soluble in ethanol, ethyl ether, acetone, chloroform and benzene [28]. As a liquid methyl acrylate is slightly less dense than water (density: 0.95 g/cm^3, water is 1.0 g/cm^3)[28], as a gas it has a much higher relative vapour density to air (vapour density 3.0 (air = 1)) [29]. Methyl acrylate is flammable, the lower flammability limit (LFL) is 2.8% v/v in air and the upper limit (UFL) is 25% v/v [30], it has a flash point of -2.8°C [31].

SDS for methyl acrylate carries the following GHS pictograms and hazard statements:

H225	Highly flammable liquid and vapour
H302 + H312	Harmful if swallowed or in contact with skin
H315	Causes skin irritation
H317	May cause and allergic skin reaction
H319	Causes serious eye irritation

H331   Toxic if inhaled

H335   May cause respiratory irritation

H412   Harmful to aquatic life with long lasting effects

5.1.2   Ethyl Acrylate

Ethyl acrylate has a 'penetrating acrid' odour [32]. It is a colourless liquid with a boiling point of 99.4°C [33].

In terms of solubility, it is described as being slightly soluble in water (1.5 g/100 ml) [34], soluble in chloroform and fully miscible in ethanol and ethyl ether [33]. As a liquid ethyl acrylate is slightly less dense than water (density: 0.92 g/cm^3, water is 1.0 g/cm^3)[34], as a gas it has a much higher relative vapour density to air (vapour density 3.45 (air = 1)) [34]. Ethyl acrylate is flammable, the lower flammability limit (LFL) is 1.8% v/v in air and the upper limit (UFL) is 12.1% v/v [35], it has a flash point of 10°C [34].

SDS for ethyl acrylate carries the following GHS pictograms and hazard statements:

H225   Highly flammable liquid and vapour

H302 + H312   Harmful if swallowed or in contact with skin

H315   Causes skin irritation

H317   May cause and allergic skin reaction

H319   Causes serious eye irritation

H331   Toxic if inhaled

H335   May cause respiratory irritation

H412   Harmful to aquatic life with long lasting effects

5.1.3   2-Ethyl-3-methylpyrazine

2-Ethyl-3-methylpyrazine is present in the gas odour-S-free mixture as a stabiliser, although it also is described has having a stench odour. It is a colourless liquid with a boiling point of 57°C (10 mm Hg) [36], equating to a value of 192°C at atmospheric pressure.

In terms of solubility, 2-ethyl-3-methylpyrazine is described as being sparingly soluble in water [37]. It is marginally less dense than water (density: 0.987 g/cm^3, water is 1.0 g/cm^3)[37]. 2-Ethyl-3-methylpyrazine is flammable and whilst no flammable limit data has been reported, it has a flash point of 58.9°C [38].

SDS for 2-ethyl-3-methylpyrazine carries the following GHS pictograms and hazard statements:

H226	Flammable liquid and vapour
H302	Harmful if swallowed
H315	Causes skin irritation
H319	Causes serious eye irritation
H335	May cause respiratory irritation

5.2   SYNONYMS OF INDIVIDUAL COMPONENTS OF GASODOR-S-FREE

5.2.1   Synonyms of Methyl Acrylate
Methylacrylate
Acrylic acid methyl ester
Methyl prop-2-enoate
2-Propenoic acid, methyl ester
 [96-33-3] CAS Number

5.2.2   Synonyms of Ethyl Acrylate
Ethylacrylate
Acrylic acid ethyl ester
Ethyl prop-2-enoate
2-Propenoic acid, ethyl ester
 [140-88-5] CAS Number

5.2.3   Synonyms of 2-Ethyl-3-methylpyrazine
BRN 0956775
Filbert pyrazine
[15707-23-0] CAS Number

5.3   HEALTH EFFECTS OF INDIVIDUAL COMPONENTS OF GASODOR-S-FREE
Methyl acrylate has an oral LD_{50} (oral-rat) of 768 mg/kg)[39], ethyl acrylate has an LD_{50} (oral-rat) of 1120 mg/kg) [40] and 2-ethyl-3-methylpyrazine has an LD_{50} (oral-rat) of 600 mg/kg)[38]. These values have been used to feed into the required CLP calculation for the mixture (Appendix A). Although health effects must be considered at the point of introduction of odorant to the gas, where the odorant is present in its concentrated form, once diluted by the bulk gas, its health effects can be discounted. It is of note that both methyl acrylate and ethyl acrylate have workplace exposure limits (Table 2) [41].

Table 2; Workplace Exposure Limits for Methyl Acrylate and Ethyl Acrylate (taken from HSE EH-40/2005)

Substance	CAS Number	Workplace Exposure Limit			
		Long-term exposure limit (8-hr TWA reference period)		Short-term exposure limit (15 minute reference period)	
		ppm	mg.m^{-3}	ppm	mg.m^{-3}
Ethyl acrylate	[140-88-5]	2	21	10	42
Methyl acrylate	[96-33-3]	5	18	10	36

5.4 ENVIRONMENTAL EFFECTS OF INDIVIDUAL COMPONENTS OF GASODOR-S-FREE

Methyl acrylate and ethyl acrylate each carry the same specific environmental hazard phrase (H412- Harmful to aquatic life with long lasting effects). However, as each component will only be present in a very dilute concentration within the bulk gas stream, any impact on the environment arising from either material can largely be discounted.

6   5-ETHYLIDENE-2-NORBORNENE

6.1   APPEARANCE / PHYSICAL PROPERTIES OF 5-ETHYLIDENE-2-NORBORNENE

5-Ethylidene-2-norbornene is a colourless liquid described has having a turpentine-like odour [42] (odour threshold 0.014 ppm [43]). It has a boiling point of 298°C [44].

In terms of solubility, 5-ethylidene-2-norbornene is described as being sparingly soluble in water [45]. It is marginally less dense than water (density: 0.9 g/cm^3, water is 1.0 g/cm^3)[45], as a vapour it has a relative vapour density significantly greater than air (vapour density 4.1(air = 1)) [45]. 5-Ethylidene-2-norbornene is flammable and whilst no flammable limit data has been reported, it has a flash point of 38°C [45].

SDS for 5-ethylidene-2-norbornene carries the following GHS pictograms and hazard statements:

H226   Flammable liquid and vapour

H304   May be fatal if swallowed and enters airways

H315   Causes skin irritation

H332   Harmful if inhaled

H373   May cause damage to organs (Liver, Testes) through prolonged or repeated exposure

H411   Toxic to aquatic life with long lasting effects

6.2   SYNONYMS OF 5-ETHYLIDENE-2-NORBORNENE

Although most generally known as 5-ethylidene-2-norbornene, it can also be known as:

5-Ethylidenebicyclo[2.2.1]hept-2-ene

[16219-75-3] (CAS Number)

6.3   HEALTH EFFECTS OF 5-ETHYLIDENE-2-NORBORNENE

5-Ethylidene-2-norbornene has an oral LD_{50} (oral-rat) of 2276 mg/kg[46]. As this value is in excess of 2000 mg/kg, the compound is not required to be evaluated by a CLP toxicity determination.

6.4   ENVIRONMENTAL EFFECTS OF 5-ETHYLIDENE-2-NORBORNENE

5-Ethylidene-2-norbornene carries a specific environmental hazard phrase (H411-Toxic to aquatic life with long lasting effects). However, due to the fact that the component will only be present in a very dilute concentration within the bulk gas stream, any impact on the environment can largely be discounted.

7   SUMMARY/CONCLUSIONS

From the evaluations performed, all of the shortlisted odorants appear to be fit-for-purpose in terms of their health and environmental impact.

Whilst care should be taken at the point of introduction of the pure, concentrated odorants, when diluted within the hydrogen gas stream at the indicated concentration all health and environmental impact of each of the odorants / odorant mixtures can be discounted.

Further dilution in the event of a leak of the odorised gas stream into air will further mitigate against any health or environmental effects.

Accordingly, all of the shortlisted odorant candidates can be considered suitable for the next stages of NPL's experimental work.

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9 APPENDIX A; CLP SUMMARY

Mixture	Id Name	CLP CLASSIFICATION As Concentrate		CLP CLASSIFICATION as odorant in Pipeline		Components		%	Conc in Pipeline		Injection rate mg/m³	Synonyms	Risk Codes	Formula	Mol Wt (g/mol)	CAS	EC - No	Tox Data					Units
1	Odorant NB	Both the components of this odourant have LD50 oral (Rat) toxicity values in excess of 2000 mg/kg, LD50 dermal (Rabbit) toxicity values in excess of 2000mg/kg and Gas inhalation Toxicity values in excess of 20000 ppmv and as such are not considered as part of a CLP toxicity determination.				Tertiary butyl mercaptan	TBM	78	1.3 µmol mol⁻¹		6	2-methyl-2-propanethiol	H225, H317, H411	$C_4H_{10}S$	90.19	75-66-1	200-890-2	LD50 Rat Oral / LC50 Rat Inhalation 4hrs / LC50 Rat Inhalation 4hrs / LD50 Rabbit Dermal				4729 / 22200 / 26643 / 2000	mg/kg / ppm / ppm / [>] mg/kg
						Dimethyl sulphide	DMS	22	0.5 µmol mol⁻¹			Methyl Sulphide	H225, H319	C_2H_6S	62.13	75-18-3	200-846-2	LD50 Rat Oral / LC50 Rat Inhalation 4 hrs / LD50 Rabbit Dermal				3300 / 102 / 5000	mg/kg / mg/l / [>] mg/kg
								100															
2	Standby Odorant	Both the components of this odourant have LD50 oral (Rat) toxicity values in excess of 2000 mg/kg, LD50 dermal (Rabbit) toxicity values in exess of 2000mg/kg and Gas inhalation Toxicity values in exess of 20000 ppmv and as such are not considered as part of a CLP toxicity determination.				Tertiary butyl mercaptan	TBM	26.52				AS ABOVE											
						Dimethyl Sulphide	DMS	7.48				AS ABOVE											
						Hexane		66					H225,H315,H319, H361f,H336,H373 ,H304,H411	C_6H_{14}	86.18	110-54-3	203-777-6	None Available					
								100															
3	Odorant THT	LD50 Rat Oral Conc 0.057 / Oral ATE mg/kg (CLP Toxic Cat 4) 1750		LD50 Rat Oral Conc 2.86E-07 / Oral ATE mg/kg (CLP TOXIC NOT CLASSIFIED) 350000000		Tetrahydrothiophene	THT	100	5 ppm		18	Tetramethylene sulfide	H225, H302, H312, H315, H319, H332, H412	C_4H_8S	88.17	110-01-0	203-728-9	LD50 Rat Oral				1750	mg/kg
								100															
4	Gasodor-S-Free	LD50 Rat Oral Conc 0.049 / LC50 Rat Inhalation Conc 3.453 / LD50 Rabbit Dermal Conc 0.030		LD50 Rat Oral Conc 1.11E-07 / LC50 Rat Inhalation Conc 7.85E-06 / LD50 Rabbit Dermal Conc 6.84E-08		Methyl acrylate	MA	37.4	0.85 ppm	3.03E-06		2-Propenoic acid methyl ester Methyl prop-2-enoate	H225, H302, H331, H312, H315,H317, H335, H412	$C_4H_6O_2$	86.09	96-33-3	202-500-6	LD50 Rat Oral / LC50 Rat Inhalation 4 hrs / LD50 Rabbit Dermal				758 / 10.832 / 1243	mg/kg / [>] mg/l / mg/kg
		LD50 Rat Oral Conc 0.054 / LC50 Rat Inhalation Conc 6.678 / LD50 Rabbit Dermal Conc 0.033		LD50 Rat Oral Conc 7.59E-08 / LC50 Rat Inhalation Conc 9.44E-06 / LD50 Rabbit Dermal Conc 4.72E-08		Ethyl acrylate	EA	60.1	1.17 ppm	4.851E-06	8	Acrylic acid ethyl ester	H225,H302,H331, H312,H315,H319, H317,H335,H412	$C_5H_8O_2$	100.12	140-88-5	205-438-8	LD50 Rat Oral / LC50 Rat Inhalation 4 hrs / LD50 Rabbit Dermal				1120 / 9 / 1800	mg/kg / mg/l / mg/kg
		LD50 Rat Oral Conc 0.004 / LC50 Rat Inhalation Conc 0.000 / LD50 Rabbit Dermal Conc 0.000		LD50 Rat Oral Conc 1.42E-07 / LC50 Rat Inhalation Conc 0.00E+00 / LD50 Rabbit Dermal Conc 0.00E+00		2-ethyl-3-methylpyrazine	EMP	2.5	0.04 ppm	2.024E-07			H226.H302,H315, H319,H335	$C_7H_{10}N_2$	122.17	15707-23-0	239-799-8	LD50 Rat Oral / LC50 Rat Inhalation 4hrs / LD50 Rabbit Dermal				600	mg/kg / mg/l / mg/kg
								100															
		Sum Oral LD50 Conc 0.107 / Sum Inhalation LC50 Conc 10.131 / Sum Dermal LD50 Conc 0.063		Sum Oral LD50 Conc 3.28E-07 / Sum Inhalation LC50 Conc 1.73E-05 / Sum Dermal LD50 Conc 1.16E-07					15 / 24 / 1	21 / 29 / 1	15 / 24 / 1												
		Oral ATE mg/kg (CLP TOXIC Cat 4) 939 / Inhalation ATE mg/l (CLP TOXIC Cat 4) 10 / Dermal ATE mg/kg (CLP TOXIC Cat 4) 1575		Oral ATE mg/kg (CLP TOXIC NOT CLASSIFIED) 304658279 / Inhalation ATE mg/l (CLP TOXIC NOT CLASSIFIED) 5783167 / Dermal ATE mg/kg (CLP TOXIC NOT CLASSIFIED) 865013242																			
5	5-ethylidene-2-norbornene	The component of this odourant has LD50 oral (Rat) toxicity values in excess of 2000 mg/kg, LD50 dermal (Rabbit) toxicity values in excess of 2000mg/kg but a vapour inhalation Toxicity of 13.5 mg/l. This would result in a CLP classification for inhalation toxicity of category 4				5-ethylidene-2-norbornene		100	17 ppm		84		H226,H332,H315, H373,H304,H411	C_9H_{12}	120.19	16219-75-3	240-347-7	LD50 Rat Oral / LC50 Rat Inhalation 4 Hrs / LD50 Rabbit Dermal				2276 / 13.5 / 7168	mg/kg / mg/l / [>] mg/kg
								100															

HEALTH & SAFETY LABORATORY

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APPENDIX C

Gravcalc files showing exact gas composition for the prepared mixtures

Odorant NB (NG812)

Component	µmol/mol	uncertainty	% u/c
H2	999997.8782	0.05454620	0.000
t-BuSH	1.51136571	0.01429138	0.946
Me2S	0.42628263	0.01272942	2.986
N2	0.07663879	0.04255440	55.526
CxHy	0.04406381	0.01397244	31.710
O2	0.04207503	0.02336256	55.526
H2O	0.00999998	0.00555258	55.526
Ar	0.00571467	0.00317312	55.526
CO2	0.00519999	0.00105791	20.344
methane	0.00037761	0.00020968	55.528
CO	0.00005815	0.00003229	55.521

Standby odorant 2 (NG817)

Component	µmol/mol	uncertainty	% u/c
H2	999997.9215	0.09923968	0.000
n-hexane	1.27937737	0.04826411	3.772
t-BuSH	0.51407709	0.04156175	8.085
Me2S	0.14499610	0.04982356	34.362
N2	0.07663879	0.04258905	55.571
O2	0.04207503	0.02338158	55.571
H2O	0.00999998	0.00555710	55.571
Ar	0.00571467	0.00317570	55.571
CO2	0.00519999	0.00105877	20.361
methane	0.00037761	0.00020985	55.573
CO	0.00005815	0.00003231	55.566

Odorant THT (NG845)

Component	µmol/mol	uncertainty	% u/c
H2	999994.8558	0.04859067	0.000
THT	4.99408201	0.01141915	0.229
N2	0.07663856	0.04009716	52.320
O2	0.04207490	0.02201352	52.320
CxHy	0.01000818	0.00499916	49.951
H2O	0.00999995	0.00523195	52.320
Ar	0.00571465	0.00298989	52.320
CO2	0.00519997	0.00099682	19.170
methane	0.00037761	0.00019757	52.321
CO	0.00005815	0.00003042	52.315

GASODOR-S-FREE (NG815)

Component	µmol/mol	uncertainty	% u/c
H2	999999.8198	0.04892738	0.000
N2	0.07669238	0.04251071	55.430
O2	0.04205829	0.02333857	55.491
H2S	0.04009933	0.00024907	0.621
H2O	0.00999600	0.00554688	55.491
Ar	0.00571240	0.00316986	55.491
CO2	0.00519792	0.00105682	20.332
methane	0.00037746	0.00020946	55.493
CO	0.00005817	0.00003225	55.448

```
OCS                    0.00003680     0.00000368     10.003
```

5-ethylidene-2-norbornene (NG846)

```
Component        µmol/mol            uncertainty      % u/c
----------------------------------------------------------
H2               999982.7253         0.05241556       0.000
5-ethylidene-2-n  17.0208718         0.02204780       0.130
CxHy              0.11374955         0.01979098      17.399
N2                0.07663763         0.03744213      48.856
O2                0.04207439         0.02055589      48.856
H2O               0.00999983         0.00488552      48.856
Ar                0.00571458         0.00279192      48.856
CO2               0.00519991         0.00093082      17.901
methane           0.00037760         0.00018449      48.858
CO                0.00005815         0.00002841      48.853
```
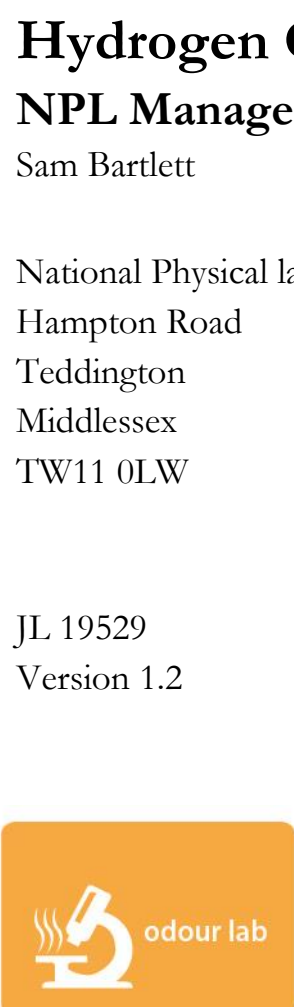
5-ethylidene-2-norbornene (NG846)

```
Component        µmol/mol            uncertainty      % u/c
----------------------------------------------------------
H2               999982.7253         0.05241556       0.000
5-ethylidene-2-n  17.0208718         0.02204780       0.130
```

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28/11/2018

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ABBREVIATIONS

ASE   Air Spectrum Environmental Limited

DDO   Dynamic Dilution Olfactometry

ODT   Odour detection threshold

OU_E/m^3 Odour units per meter cubed

SES   Spectrum Environmental Support

EXECUTIVE SUMMARY

Due to the subjective nature of odour, the report is split into several parts, odour threshold concentration analysis, Hedonic Tone, Odour Intensity and Odour character.

Human panel members have been used for all of the testing carried out in this programme of analysis. However, all panellists are classified as "Trained assessors" having specific odour acuity in accordance with EN13725 dynamic dilution olfactometry.

In terms of the odour detection threshold concentration results, Odorant NG 812 has the highest odour detection threshold with Odorant NG846 having the lowest odour detection threshold concentration. Odour detection threshold concentration is a quantitative measurement of how strong an odour is. Odorant NG 812 had an odour detection threshold concentration of 148,361 which was greater than the next strongest odorant (NG 817 – 73,211) by more than a factor of 2.

Odour intensity is related to odour detection threshold concentration but is a subjective measure of the perceived strength of a particular odour above its odour detection threshold. The key criteria that was being assessed by the odour intensity element of the testing, was to identify if the respective odorants were perceived as a medium odour intensity according to the Sales scale. The assessment results indicate that all of the odorants were perceived as a medium odour intensity in their dilute form. However, some odorants were perceived as more intense than others across a range of dilution levels. Odorant NG 812 was by far the most intense odorant and could be perceived as a medium intensity odour at dilutions in excess of 40,000 (on average).

Hedonic tone results are a subjective measurement of an odour's pleasantness or unpleasantness based upon a scale of positive 4 to negative 4 with 0 as neutral. Sample NG817 presented the highest average negative response with NG812 a close second position, however sample NG 845, 846 and 815 presented fairly neutral to positive responses. If the Hedonic tone is considered alongside the odour character results, it can be seen that NG812 presented negative responses possibly due to the sulphur nature of the odour, with NG817 presenting a wide range of odour character.

The overall aim of the assessment was to identify the most suitable stenching agent in terms of:

- Are the odorants of a suitable strength (odour concentration) to be easily detected.

- Can the odorant be detected at a suitable intensity (Sales scale of 2 – medium intensity) to alert people of a potential gas leak

- Do the odorants have a distinct unpleasant character so that they can be distinguishable from other common odours.

Each odorant met the test criteria in terms of being of sufficient strength and intensity to alert people of a possible gas leak.

However not all of the odorants were perceived as unpleasant.

Taking the above three critical factors in to consideration, the table below illustrates the suitability of each odorant

Odorant suitability

ODORANT	COMPONENT	AMOUNT/FRACTION (µmol/mol)
Ng 812	2-methyl-propanethiol Dimethyl Sulphide	1.51 0.426
NG 817	Hexane 2-methyl-propanethiol Dimethyl Sulphide	1.28 0.514 0.145
NG 845	5-ethylidene-norbornene	17.0
NG 815	Ethyl acrylate Methyl acrylate 2-ethyl-3methylpyrazine	1.124 0.699 0.047
NG 846	Tetrahydrothiophene	4.99

Suitability Key: [green]   **= all criteria passed**

           [orange]   **= all criteria passed except for unpleasantness criteria**

1.0 INTRODUCTION
1.1 Background

The National Physical laboratory commissioned Air Spectrum Environmental ltd to carry out a programme of testing on five different odorants to assess their suitability for use as stenching agents in a hydrogen gas network trial.

1.2 Scope of works

Air Spectrum Environmental Ltd were tasked with assessing the suitability of five different odorants as stenching agents as part of a hydrogen gas network trial.

The following key performance criteria were to be assessed for each odorant:

- Determination of the odour detection threshold concentration – This is a measure of the relative strength of each odorant.

- Assessment of the odour intensity of each odorant with focus on whether the odorants can be perceived as a medium odour intensity (Sales scale – Olfactory degree 2).

- Determination of the Hedonic tone of each gas odorant to assess their relative pleasantness / Unpleasantness.

- Assessment of the odour character of each odorant to determine what type of odour each odorant is perceived to have and also whether the odorants have a distinct character.

1.3 Limitations

ASE has prepared this report for the sole use of the client, showing reasonable skill and care for the intended purposes as stated in the agreement under which this work was completed.

The report may not be relied upon by any other party without the express agreement of the client. No other warranty, expressed or implied is made as to the professional advice included in this report.

Where any data supplied by the client or from other sources have been used, it has been assumed that the information is correct. No responsibility can be accepted by ASE for inaccuracies in the data supplied by any other party. The conclusions and recommendations in this report are based on the assumption that all relevant information has been supplied by those bodies from whom it was requested.

This work has been undertaken in accordance with the Safety, Health, Environmental and Quality Management System of ASE.

2.0 LEGISLATION AND POLICY

2.1 Odour definition

The majority of **odours** consist of a **complex combination of chemicals** which are released in to the air. Reaction of the olfactory nerve in response to odour, results in perception of smell. Odours can be detected and identified at very low concentrations. The response by sensitive receptors is highly subjective as everyone has a unique set of cells. Odours can be perceived as either neutral, pleasant/acceptable, or unpleasant/unbearable. This strictly depends on several factors such as; genetics (e.g. sensitivity, odour tolerance threshold), first-hand experiences (e.g. memories, living environment), cultures. Odours can be transported at long distances via atmospheric circulation and thus have an impact on the wider population.

2.2 Odour assessment techniques

Odour assessment techniques can measure a variety of properties that an odour may possess. The key odour parameters that are measured in this assessment are outlined below

Odour threshold concentration

Odour concentration is defined as the number of odour units per meter cubed of air (ou_E/m^3) and is one way of expressing the relative strength of an odour. Odour concentration measurements are based on the odour detection threshold of an odour which is the dose of odorant that 50% of the population will detect as a sensory stimulus. Within Olfactometry, the detection threshold of an odour has been calibrated equal to 123 µg of n-butanol evaporated in 1 m^3 of neutral odour free air. Odour concentrations are therefore calculated as a multiple of the detection threshold. The multiple is equal to the dilution factor required to achieve the dilution threshold. The ou_E/m^3 represents the number of times a sample can be diluted and still be detected, therefore the higher the measurement the more concentrate the sample odour.

Odour Intensity

Odour intensity is a measure of the perceived strength of an odour above its threshold. It is measured by a panel of trained assessors using a reference scale to assess the intensity.

Hedonic tone

Hedonic tone is a measure of the relative pleasantness or unpleasantness of an odour. A panel of trained assessors are presented with the odour at various dilutions above threshold and assess the pleasantness of the odour using the reference hedonic tone scale.

Odour Character

The character of an odour is essentially what the odour smells like and allows people to distinguish it from other types of odour. Odour character is determined by presenting the raw or dilute odour to a group of acuity certified panellists who describe the type and nature of the smell using pre-defined descriptive words.

2.3 Gas Odorant regulations

Odorants are added to natural gas and other gaseous fuels for reasons of public safety so as to enable the detection of possible gas leaks.

The Gas Safety (management) regulations (GS(M) R) 1996, place a formal obligation on agencies involved in the supply and transport of natural gas to ensure that the gas is treated with a suitable stenching agent which imparts a distinct odour on the treated gas and will also impart a distinct odour if the treated gas is mixed with a non - treated gas.

This regulation would also apply to alternatives to natural gas that are used in the public gas supply network.

The regulations also stipulate that the character of the odour should be distinguishable from other smells such as sewer type odours.

The odorant should also be added at a concentration at which it can be detected at an intensity of 2 on the Sales scale. This is thought to guarantee that a leak can be detected well before the gas concentration in air reaches the lower flammability limit.

3.0 METHODOLOGY
3.1 Odour threshold analysis

On the day of the testing, each gas sample was transferred directly from the gas cylinders to an inert Nalophan sample bag. Triplicate samples were collected for each odorant.

Each sample was processed within two hours of its collection to determine its odour detection threshold. The average of the three odour detection threshold measurements determined for each gas odorant was then calculated.

Odour threshold is a measurement of the concentration for an odorous gas. The measurement is achieved by presenting a dilution range of the test gas to a panel of acuity assessed panellists. Panellists vote whether they can detect an odour or not at each dilution range presented, from these responses the detection point is established. The detection point is the dilution at which 50% of the panel can detect an odour which in turn represents an odour concentration of $1ou_E/m^3$. The test sample odour concentration is calculated by multiplying the detection concentration (1 ou_E/m^3) by the dilution factor required to achieve the detection point. Odour threshold analysis was measured in accordance with BS EN 13725:2003[1] at Odour Laboratory, a UKAS accredited laboratory (#8283).

3.2 Odour intensity analysis
Once the average odour detection threshold concentration was determined for each gas odorant, the odour intensity could then be measured. Each gas odorant sample was presented at increasing concentrations starting at a concentration just above its odour detection threshold to a group of acuity certified panellists. The Scentroid SS600 Olfactometer was used to present the diluted samples at a controlled flow rate through one sniff port.

During the presentation of the sample at each concentration point, the panellists were asked to assess the perceived intensity using the following scale:

TABLE 1 – Sales odour intensity scale

Intensity Scale (Olfactory degree)	Perceived sensation
0	No odour
0.5	Very feeble odour (Odour detection threshold)
1	Feeble odour
2	Medium odour (alert level)
3	Strong odour
4	Very strong odour
5	Maximum odour

---

[1] BS EN 13725:2003. Air Quality – Determination of odour concentration by dynamic olfactometry.

The perceived intensity measurements from the panellists were carried out in triplicate for each gas odorant. The average odour intensity at each concentration/ dilution point is presented in the results section

3.3 Hedonic Tone

Once the Odour threshold concentration (ODT) was established for each gas odorant, triplicate hedonic tone measurements were performed for each odorant.

Hedonic tone measurements were performed by presenting each gas odorant above the respective odour detection thresholds using a Scentroid SS600 Olfactometer, to a group of acuity certified panellists.

In Hedonic tone mode, the olfactometer presents the odorant at random dilutions (above ODT) mixed with two control blanks (fresh air), through one port. Each panel member then rates the relative unpleasantness / pleasantness of the sample using the reference hedonic tone scale as displayed in table 2 below.

TABLE 2 – Hedonic tone scale

Hedonic tone classification	Perceived pleasantness / unpleasantness
+4	**Very pleasant**
+3	**pleasant**
+2	**Moderately pleasant**
+1	**Mildly pleasant**
0	**Neutral / no odour**
-1	**Mildly unpleasant**
-2	**Moderately unpleasant**
-3	**Unpleasant**
-4	**Very unpleasant**

The hedonic tone results are presented in section 4.3 of this report.

3.4 Odour character

The assessment of the Character of each gas odorant was measured by presenting the odorant at a controlled flow rate through one sniff port to a group of acuity certified panellists.

Each individual odorant was presented to the panel at the following dilutions in triplicate.

Table 3 – Odour character Dilution presentation steps

ODOUR CHARACTER DILUTIONS STEPS
Raw gas odorant
Gas odorant diluted by 250:1
Gas odorant diluted by 500:1

During each 20 second presentation, the panellists were asked to describe the type and nature of the odour they perceived.

The results of the odour character assessment are presented in section 4. Only Raw gas results have been presented.

4.0 ODOUR ASSESSMENT RESULTS

4.1 Odour detection threshold analysis results

The odour detection threshold concentration results for each odorant are displayed in table 4 and figure 1 below.

Table 4: Hydrogen gas odorants – Odour detection threshold concentration results

Hydrogen gas odorant reference	Analysis Date	Odour threshold concentration results – ou_E/m^3			
		A	B	C	Geometric mean
NG 817	24/10/2018	68321	71333	80157	**73,211.2**
NG 845	24/10/2018	64900	49564	50723	**54,643.5**
NG 812	24/10/2018	169116	132683	145532	**148,360.9**
NG 846	24/10/2018	22594	16927	23485	**20,786.8**
NG 815	24 & 25/10/2018	30160	35866	23474	**29,392.3**

ODORANT	COMPONENT	AMOUNT/FRACTION (µmol/mol)
Ng 812	2-methyl-propanethiol Dimethyl Sulphide	1.51 0.426
NG 817	Hexane 2-methyl-propanethiol Dimethyl Sulphide	1.28 0.514 0.145
NG 845	5-ethylidene-norbornene	17.0
NG 815	Ethyl acrylate Methyl acrylate 2-ethyl-3methylpyrazine	1.124 0.699 0.047
NG 846	Tetrahydrothiophene	4.99

The odour detection threshold concentration results for the odorants tested indicate that NG 812 is the strongest odorant in terms of odour concentration. The odour detection threshold concentration of NG 812 (148,361 ou_E/m^3) is more than twice the strength of the next strongest odorant (NG 817 – 73,211 ou_E/m^3).

The weakest odorant in terms of odour detection threshold concentration is NG 846 which had an odour detection threshold concentration of 20,787 ou_E/m^3.

Figure 1 below illustrates the odour detection threshold concentration of each of the gas odorants tested. The chart helps to illustrate the relative odour detection threshold concentrations of each gas odorant.

Figure 1 – Comparison of the Geometric mean odour detection thresholds for each Odorant
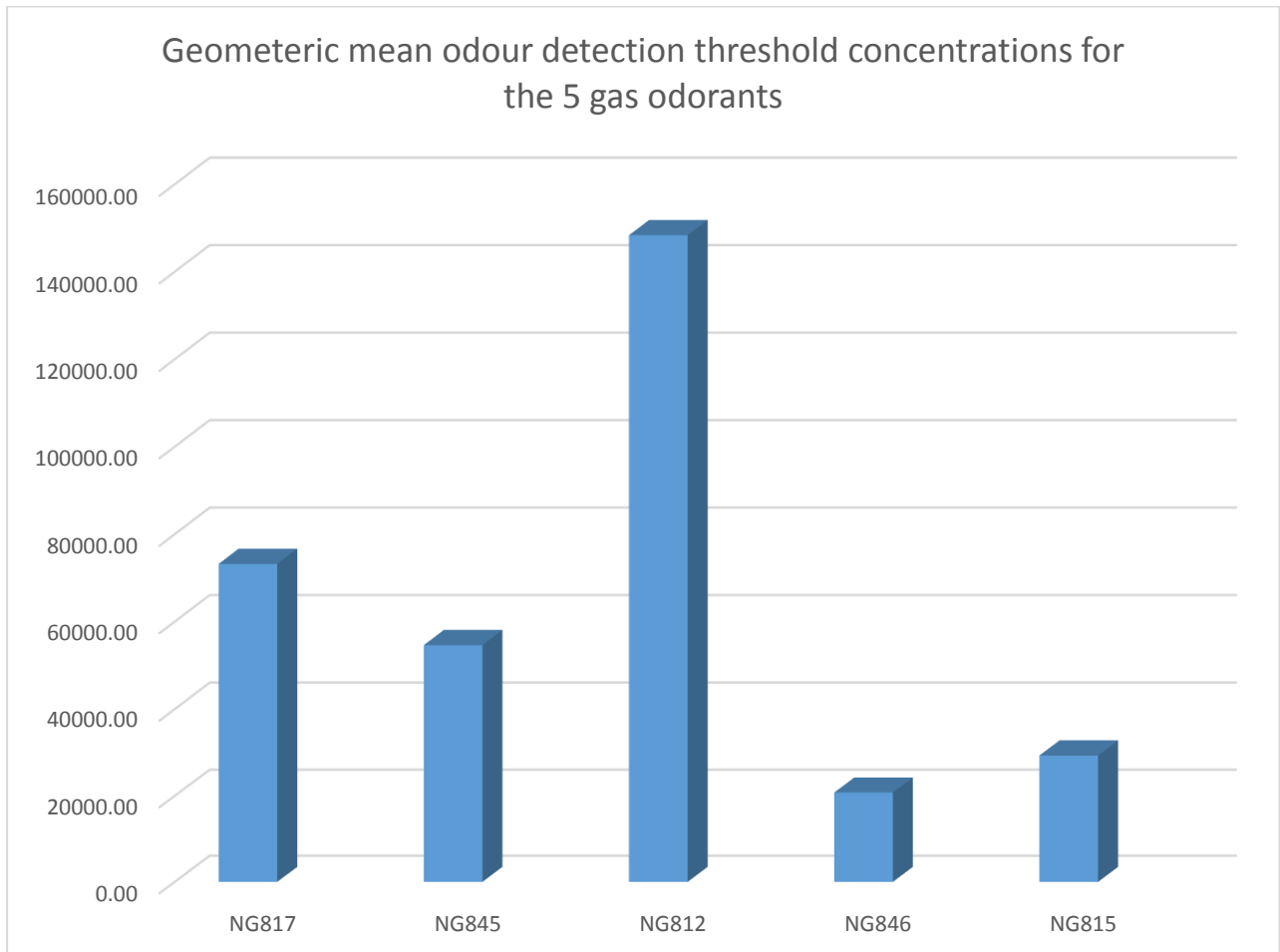
The odour detection threshold results clearly illustrate that Odorant NG 812 is the strongest.

4.2 Odour intensity results

The odour intensity results for each odorant indicates the dilution point at which, a medium odour intensity (**Sales scale: 2 – medium odour**) is perceived by the group of certified panellists. The odour intensity results for each odorant indicate at what dilution point the 1st panellist, 50% of the panellists & 100% of the panellists perceived a medium odour intensity.

Tables 5 – 9 present the odour intensity results for each odorant tested.

Table 5: Odorant NG817 - Odour intensity results

Percentage of panellists detecting an odour intensity of 2 (Medium Odour)	Dilution points			
	Round 1	Round 2	Round 3	Geometric mean
Dilution point at which **1st panellist** perceives the odour at an intensity of **2**	30.019	30,019	30,019	30,019
Dilution point at which **50% of panellists** perceives the odour at an intensity of **2**	12,255	19,186	19186	16,523
Dilution point at which **100 % of the panellists** perceives the odour at an intensity of **2**	7,834	12,255	12,255	10,557

Table 6: Odorant NG815 - Odour intensity results

Percentage of panellists detecting an odour intensity of 2 (Medium odour)	Dilution points			
	Round 1	Round 2	Round 3	Geometric mean
Dilution point at which **1st panellist** perceives the odour at an intensity of **2**	10106	5638	1752	12274
Dilution point at which **50% of panellists** perceives the odour at an intensity of **2**	32451	5638	3144	4641
Dilution point at which **100 % of the panellists** perceives the odour at an intensity of **2**	5638	3144	979	1754

Table 7: Odorant NG845 - Odour intensity results

Percentage of panellists detecting an odour intensity of 2 (Medium odour)	Dilution points			
	Round 1	Round 2	Round 3	Geometric mean
Dilution point at which **1st panellist** perceives the odour at an intensity of **2**	14688	14688	14688	14688
Dilution point at which **50% of panellists** perceives the odour at an intensity of **2**	9455	9455	9455	9455
Dilution point at which **100 % of the panellists** perceives the odour at an intensity of **2**	9455	9455	3917	7048

Table 8: Odorant NG812 - Odour intensity results

Percentage of panellists detecting an odour intensity of 2 (Medium odour)	Dilution points			
	Round 1	Round 2	Round 3	Geometric mean
Dilution point at which **1st panellist** perceives the odour at an intensity of **2**	58,269	58,269	149,105	79,700
Dilution point at which **50% of panellists** perceives the odour at an intensity of **2**	58,269	36,418	36,418	42,595
Dilution point at which **100 % of the panellists** perceives the odour at an intensity of **2**	36,418	22,768	36,418	31,140

Table 9: Odorant NG 846- Odour intensity results

Percentage of panellists detecting an odour intensity of 2 (Medium odour)	Dilution points			
	Round 1	Round 2	Round 3	Geometric mean
Dilution point at which **1st panellist** perceives the odour at an intensity of **2**	8,155	13,127	8,155	9,557
Dilution point at which **50% of panellists** perceives the odour at an intensity of **2**	8,155	8,155	4,842	6,854
Dilution point at which **100 % of the panellists** perceives the odour at an intensity of **2**	3,152	3,152	3,152	3,152

All of the odorants tested, were perceived as a medium intensity odour (Sales scale of 2) in their diluted form. However, some of the odorants were perceived as a medium odour intensity at much higher dilution points (i.e. in a less concentrated form). So, at a given concentration, some odorants are perceived as more intense odours than others.

Figures 2 – 4 compares the relative odour intensity of each gas odorant in terms of:

- At what dilution point 50% of the panellists detected a medium intensity for the respective odorants (Figure 2)
- At what dilution point 100% of the panellists detected a medium intensity for the respective odorants (Figure 3)
- The average measured odour intensity at increasing dilution levels (Figure 4)

FIGURE 2:

Air Spectrum Environmental Limited | Spectrum Environmental Support
Spectrum House | Checketts Lane | Checketts Lane Ind Est | Worcester | WR3 7JW | UK
www.airspectrum.com | +44 1905 362 100
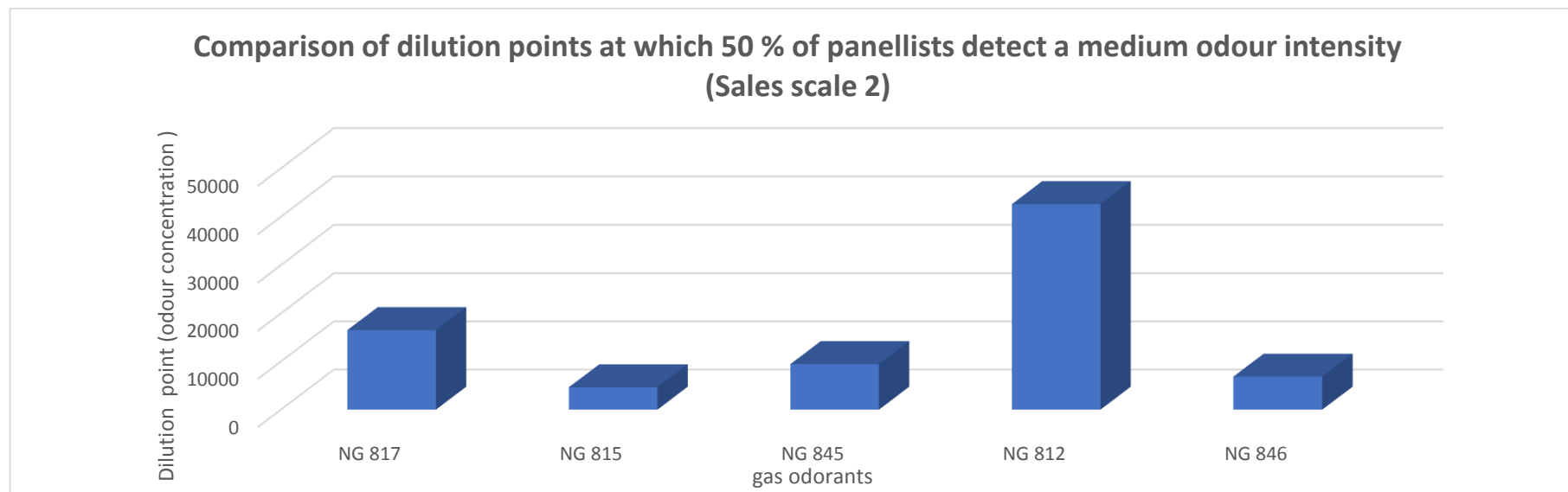
Figure 3: Comparison of dilution points at which each odorant is detected as a medium intensity by 100 % of the panellists
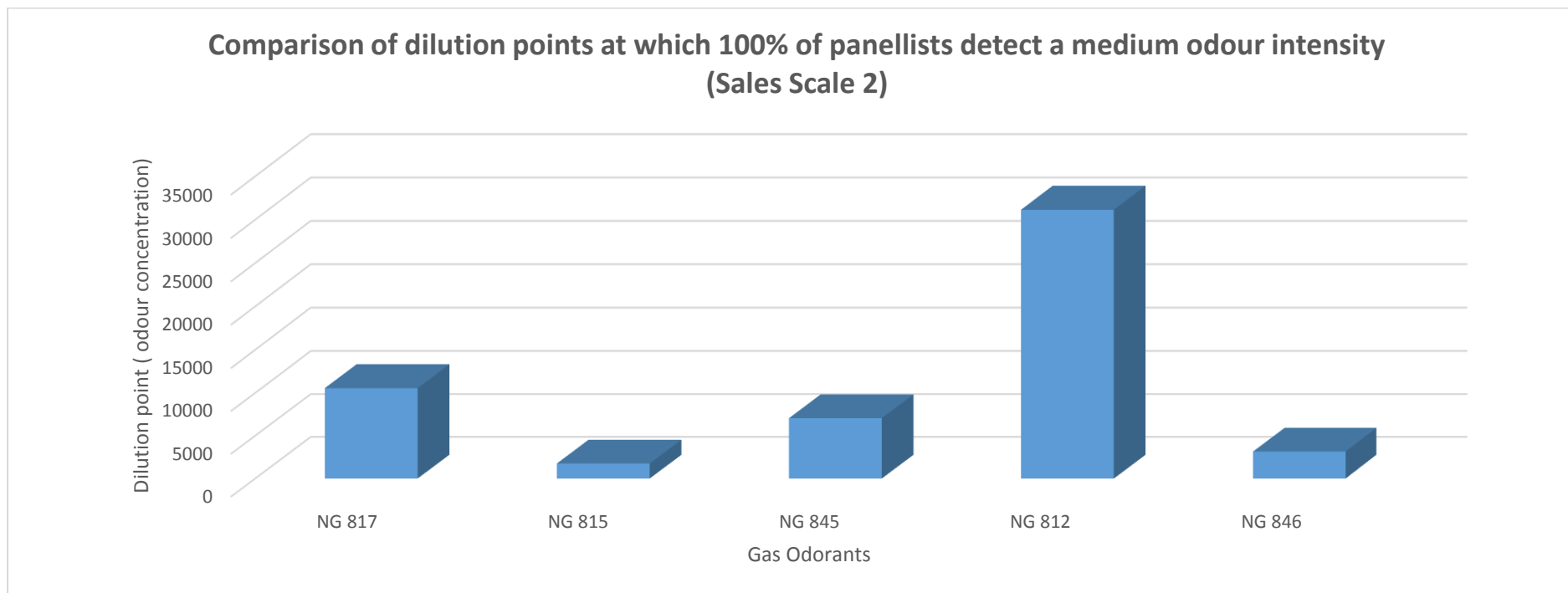
Out of all the Gas odorants, NG 812 was perceived at a medium intensity (Sales scale 2) at the lowest concentration (i.e. highest dilution point- 31,140 dilutions).

Figure 4 below, presents the average measured odour intensity score (Sales scale) recorded by the panellist group for each odorant at increasing dilution levels (i.e. decreasing actual odorant concentration).

Figure 4. Average odorant intensity results at increasing dilutions.
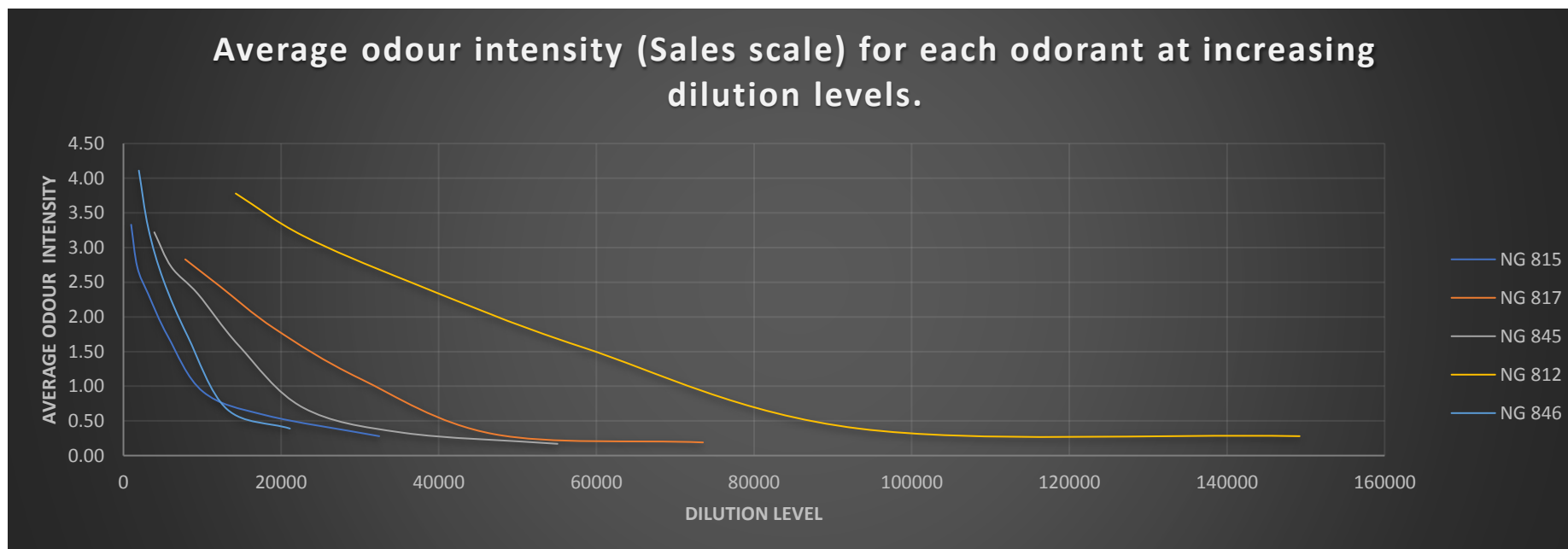
The chart above indicates that odorant NG 812 has the highest odour intensity.   Odorant NG 812 is the only odorant to be perceived at a medium odour intensity at a dilution of 40,000:1. The second most intense odorant (NG 817) could only be perceived at a medium odour intensity at a dilution level just below 20,000. Odorant NG 812 is also the only odorant that can be perceived as a faint odour at dilution levels above 60,000.

4.3 Hedonic tone results

The hedonic tone assessment results for each gas odorant is presented in the tables below (Tables 10 – 14). Each gas sample was presented to the sensory panel above the threshold of detection in accordance with VDI 3882.

NG812: Hedonic tone analysis results

Table 10

NG812		Average Hedonic Tone					
Panellist ID	OUE (dilution level)	ODL 91	ODL 096	ODL 082	ODL 141	ODL 088	ODL 132
	14234	-4	-2	-3	-1	-2	-3
	22768	-4	0	-3	0	-3	-2
	36418	-3	-2	-2	1	-1	-1
	58269	-3	0	-2	1	0	-1
	93213	-2	-1	-1	0	-1	0
	149105	-2	-1	-1	1	-1	0

Fig 5

Behaviour Curve of the Hedonic Odour Tone as a function of odourant concentration (NG 812 Average)

4 Extremely Pleasant

0 Neither Pleasant nor Unpleasant

-4 Extremely Unpleasant
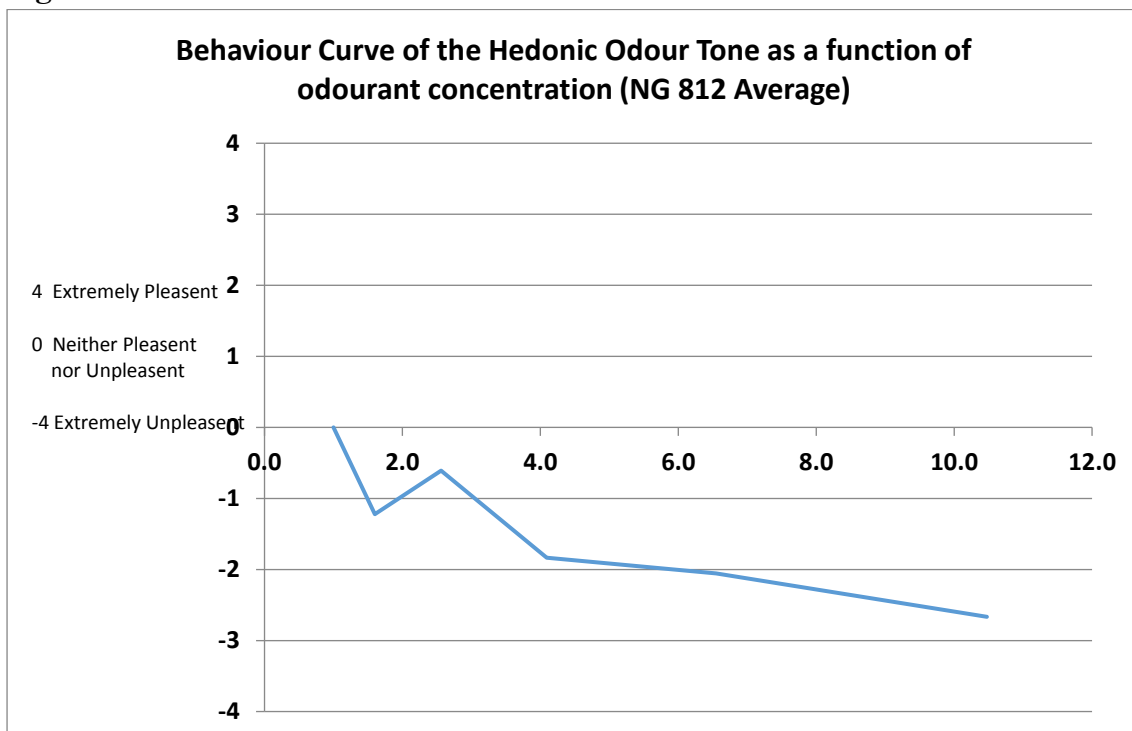
NG815: Hedonic tone analysis results

Table 11

NG815		Average Hedonic Tone					
Panellist ID	OUE (Dilution level)	ODL 91	ODL 096	ODL 082	ODL 141	ODL 088	ODL 132
	1958	-4	-2	2	-1	0	-2
	3435	-4	-2	1	-1	0	-2
	6021	-3	0	1	0	0	-2
	10557	-1	0	1	1	1	-1
	18505	0	1	0	1	0	0
	32451	0	0	0	0	0	0

Fig 6

Behaviour Curve of the Hedonic Odour Tone as a function of odourant concentration (NG 815 Average)

4 Extremely Pleasant

0 Neither Pleasant nor Unpleasant

-4 Extremely Unpleasent
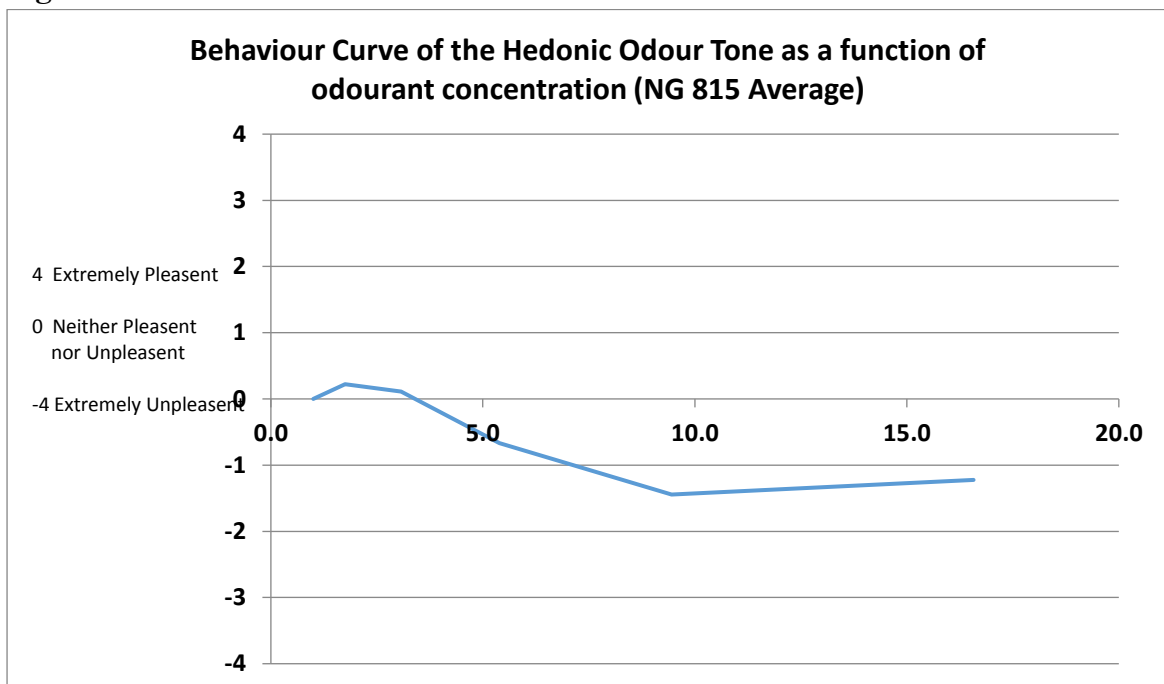
NG817: Hedonic tone analysis results

Table 12

NG817		Average Hedonic Tone					
Panelist ID	**OUE (Dilution level)**	**ODL 091**	**ODL 096**	**ODL 082**	**ODL 141**	**ODL 088**	**ODL 132**
	3917	-4	-2	-3	-1	-3	-3
	7038	-3	-2	-2	-1	-2	-3
	12661	-4	0	-1	0	-1	-2
	22751	-3	-1	-1	1	0	-1
	40897	-2	-1	-1	0	0	-2
	73524	-2	-1	-1	0	0	-1

Fig 7

Behaviour Curve of the Hedonic Odour Tone as a function of odourant concentration (NG 817 Average)

4 Extremely Pleasant

0 Neither Pleasant nor Unpleasant

-4 Extremely Unpleasant
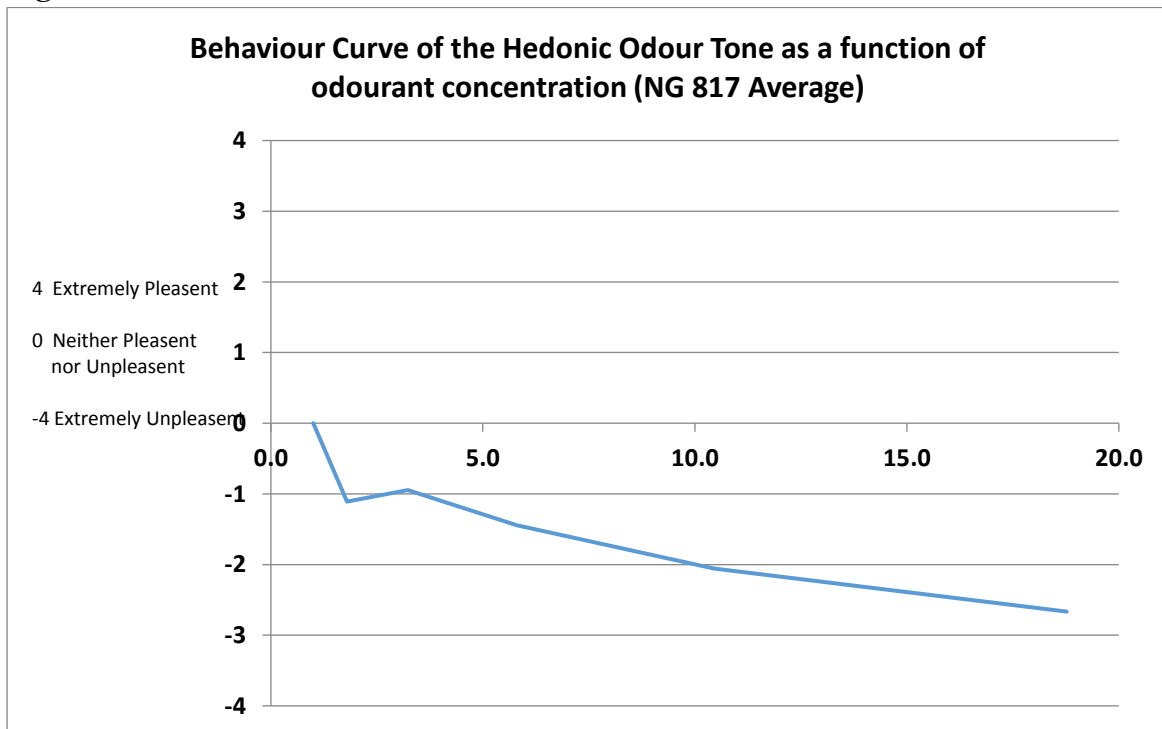
NG845: Hedonic tone analysis results

Table 13

NG845		Average Hedonic Tone					
Panellist ID	OUE (Dilution level)	ODL 91	ODL 096	ODL 082	ODL 141	ODL 088	ODL 132
	3917	4	3	2	1	2	-1
	6648	4	2	1	-1	2	1
	11276	4	2	1	1	1	1
	19133	3	2	1	3	1	1
	32459	1	1	0	1	0	1
	55065	0	1	0	0	0	1

Fig 8

Behaviour Curve of the Hedonic Odour Tone as a function of odourant concentration (NG 845 Average)
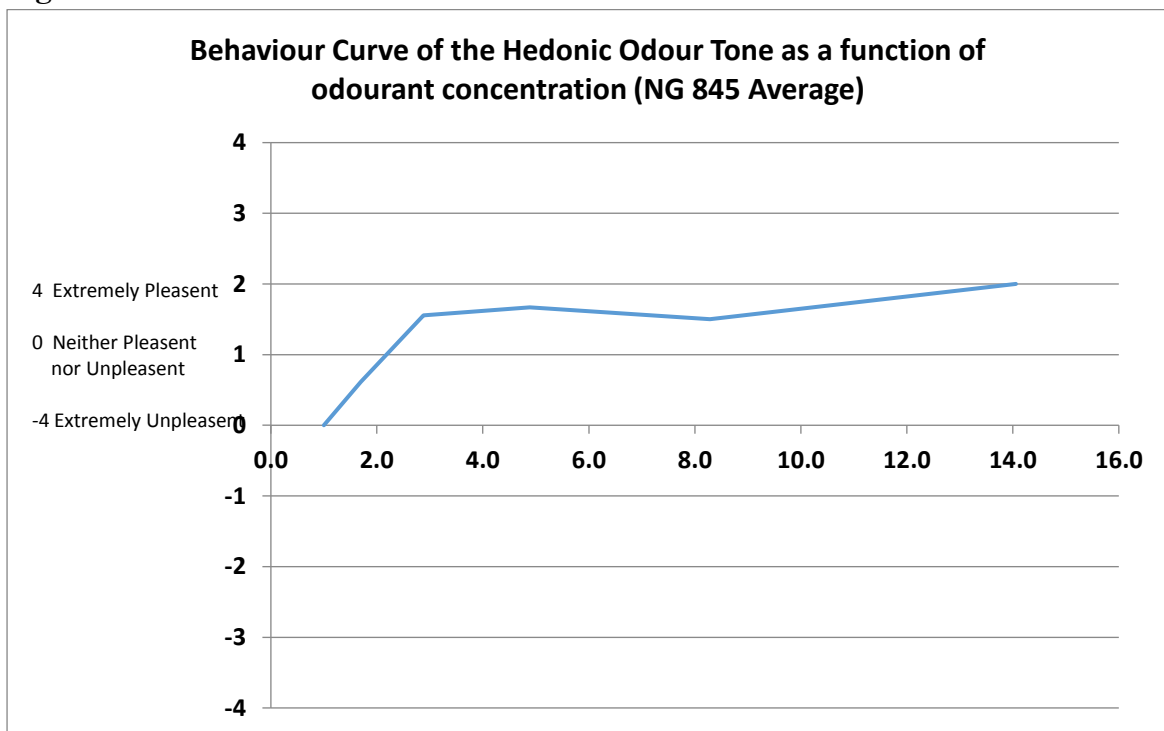
NG846: Hedonic tone analysis results

Table 14

NG846		Average Hedonic Tone					
Panelist ID	OUE (Dilution level)	ODL 91	ODL 096	ODL 082	ODL 141	ODL 088	ODL 132
	1958	3	-3	0	-2	-2	-4
	3152	3	-2	1	-3	-1	-3
	5072	1	-2	1	-1	-2	-1
	8155	1	-1	1	-1	-1	-1
	13127	0	1	0	1	0	-1
	21122	0	1	0	1	0	0

Fig 9

Behaviour Curve of the Hedonic Odour Tone as a function of odourant concentration (NG 846 Average)

4 Extremely Pleasent

0 Neither Pleasent nor Unpleasent

-4 Extremely Unpleasent
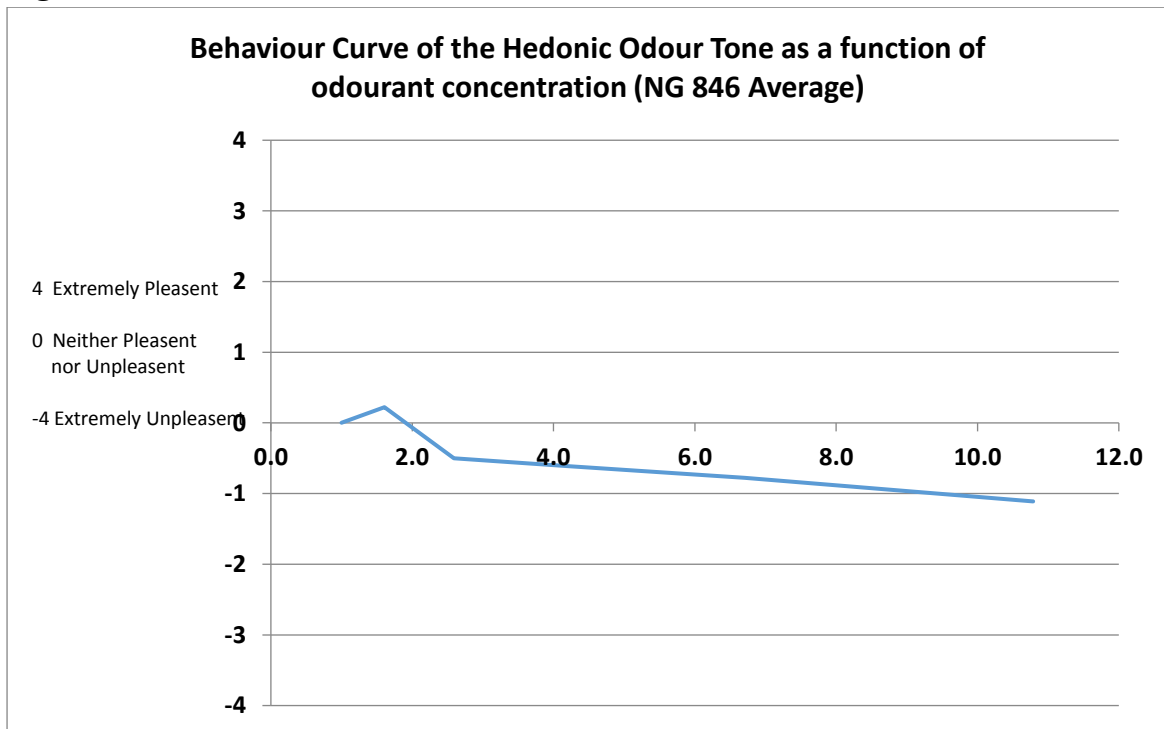
4.4 Odour Character results

NG817: Odour Character analysis results
Table 15

Raw Gas	NG817
Descriptor	Frequency
Onion	2
Petroleum	1
Rotten Egg	1
Smokey	1
Sulphur	6

Raw Gas NG817

A bar chart showing frequency values: Onion 2, Petroleum 1, Rotten Egg 1, Smokey 1, Sulphur 6.

NG845: Odour Character analysis results
Table 16

Raw Gas	NG845
Descriptor	Frequency
Fruity	2
Oil	5
Smokey	2
Sulphur	2

Raw Gas NG845

A bar chart showing frequency values: Fruity 2, Oil 5, Smokey 2, Sulphur 2.

NG812: Odour Character analysis results
Table 17

Raw Gas	NG812
Descriptor	Frequency
Grease	1
Musty	2
Oil	3
Sulphur	2
Tar	3

Raw Gas NG812

Grease	Musty	Oil	Sulphur	Tar
1	2	3	2	3
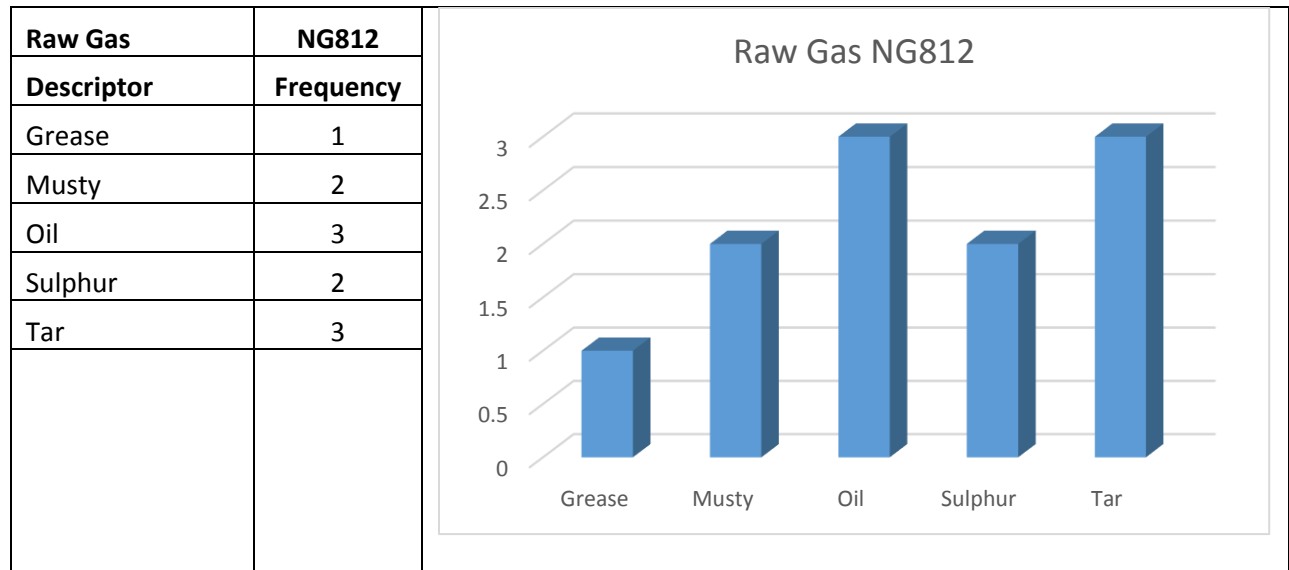
NG846: Odour Character analysis results
Table 18

Raw Gas	NG846
Descriptor	Frequency
Amine	1
Dead fish	1
Garlic	1
Mushroom	1
Musty	2
Onion	2
Petroleum	1
Solvent	1
Vomit	2

Raw Gas NG846

Amine	Dead fish	Garlic	Mushroom	Musty	Onion	Petroleum	Solvent	Vomit
1	1	1	1	2	2	1	1	2

NG815: Odour Character analysis results
Table 19

Raw Gas	NG815
Descriptor	**Frequency**
Garlic	2
Musty	1
Oil	4
Onion	2
Smokey	2
Sulphur	1

Raw Gas NG815
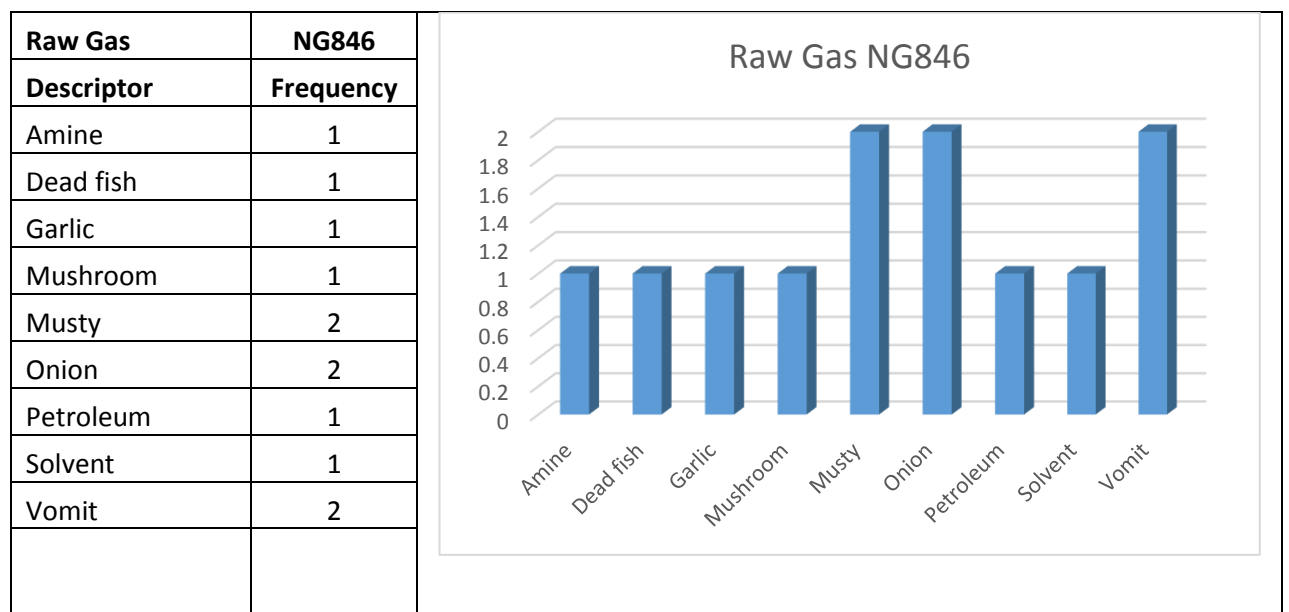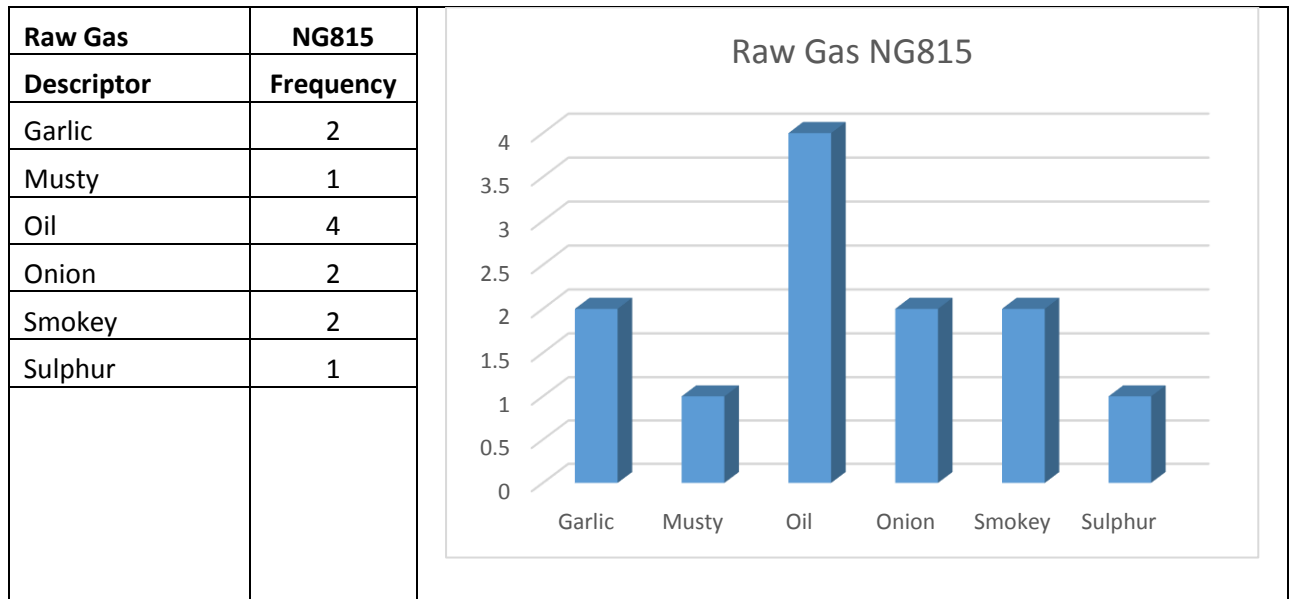
Descriptor	Frequency
Garlic	2
Musty	1
Oil	4
Onion	2
Smokey	2
Sulphur	1

PRELIMINARY SCREENING OF CANDIDATE ODORANTS FOR THE HYDROGEN GAS GRID: IMPACT ON PIPELINE INTEGRITY

JAMES HESKETH AND GARETH HINDS

JUNE 2019

Preliminary screening of candidate odorants for the hydrogen gas grid:
impact on pipeline integrity

James Hesketh and Gareth Hinds
Electrochemistry Group

EXECUTIVE SUMMARY

Preliminary screening of five different candidate odorants for use in a potential future hydrogen gas grid was carried out to assess their compatibility with existing gas network pipeline materials. Slow strain rate testing of two representative pipeline materials (PE80 polymer and X42 steel) in hydrogen was carried out in the absence and presence of the odorants. Baseline tests confirmed that neither material was susceptible to environment assisted cracking in the presence of hydrogen at ambient pressure (PE80 polymer) and up to 7 barg (X42 steel). The results of the screening tests demonstrated that none of the odorants exhibited any detrimental effect on the resistance of either material to environment assisted cracking under these conditions.

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Approved on behalf of NPL by
Dr Fernando Castro, Head of Materials Science & Engineering

CONTENTS

1. INTRODUCTION

The UK government is committed to reducing greenhouse gas emissions; with a target for 2050 of reducing emissions by 80% from the 1990 levels.[1] As highlighted in the UK's Clean Growth Strategy, the low carbon economy in the UK could grow by 11% between 2015 and 2030.[2] The UK gas infrastructure currently supplies natural gas to homes and industry. Carbon emissions are already being reduced by introducing biomethane into the mix but with new technologies becoming available for efficient and renewable hydrogen production a 100% hydrogen grid is possible and would contribute significantly towards meeting the UK 2050 emissions target. An additional factor is that the UK gas network is currently undergoing a major retrofit, with 90% of the conventional steel pipelines being replaced by polyethylene by 2032.[3]

In order to establish whether a scenario such as the 100% hydrogen gas grid is feasible, work is required to understand the potential impact on the integrity of existing infrastructure. It is well established that hydrogen can have a detrimental effect on the resistance of materials to environment assisted cracking, although this is typically only observed for high strength steels in the presence of relatively high partial pressures of hydrogen. At the relatively low pressures encountered in the gas distribution network it is considered unlikely that low strength pipeline materials such as carbon steel and polyethylene could undergo environment assisted cracking due to hydrogen. However, use of these materials under such conditions has not previously been validated and appropriate qualification testing is required.

For safety reasons, natural gas in the UK gas network is injected with an odorant that can be detected via the human olfactory system at less than 20% of the lower flammability limit of the gas.[4] This established system quickly alerts any user to a leak of natural gas; it is simple but effective. Hydrogen is a colourless, odourless, hazardous material that has a wide flammability window (4 – 74%) and can permeate through tiny leaks. Hydrogen production methods (commonly steam methane reforming or electrolysis) do not, as part of the process, introduce controlled amounts of odorant into the gas, and therefore an odorant would need to be added downstream. It is possible that existing odorants used within the natural gas grid may be suitable in a 100% hydrogen grid; however, extensive testing needs to be performed beforehand as, for example, the odorant may not behave the same way in hydrogen compared to natural gas.

As part of the SGN funded Hydrogen 100: Hydrogen Odorants and Leak Detection project, NPL performed a review of relevant standards and regulations to provide suitability criteria for an odorant that can be used within the UK's 100% hydrogen gas grid.[5] This yielded a recommendation of five potential candidates, as chosen by SGN, to be evaluated according to the following criteria:

- Olfactory characterisation
- Fuel cell degradation
- Pipeline degradation (both metallic and polymer materials)
- Boiler corrosion
- Stability
- Health and environmental effects

This report details the results of preliminary screening of the five candidate odorants based on their compatibility with pipeline materials in the UK's existing gas distribution network. X42 carbon steel and PE80 polymer were selected as representative pipeline materials. Evaluation is based on the results obtained by slow strain rate testing (SSRT) to assess the susceptibility of each material to environmentally assisted cracking in the presence of pure hydrogen (as a baseline) and in the presence of each candidate odorant gas mixture.

2. EXPERIMENTAL

2.1 TEST SPECIMENS

Steel specimens were manufactured from X42 carbon steel plate (see Appendix A for material certification, NPL reference AJHH) as shown in Figure 1. Ideally, pipeline grade X65 steel would have been used but it is only available as pipeline and is therefore difficult to source in the small quantities required for laboratory testing. As a result, X42 steel was used as a substitute for X65 due to its comparable chemical composition and mechanical properties and the fact that it can be readily ordered in plate form. Specimens had a gauge length of 80 mm, a width of 4 mm and a thickness of 4 mm. The steel specimens were loaded using pull-rods with a standard hole and pin configuration.

Figure 1: X42 carbon steel tensile specimens.

Polymer dog-bone specimens were prepared from a section of PE80 pipeline provided by John Davidson (Pipes) Ltd., as shown in Figure 2. Specimens had a gauge length of 15 mm, a width of 3 mm and thickness of 3 mm. It was originally intended to use a different design involving much larger cylindrical specimens. The advantage of using larger specimens is that they are easier to grip when applying tensile loading, and the larger forces involved can be measured with greater precision. However, due to constraints associated with material supply, the design had to be changed to a smaller specimen to allow for timelier and more cost-effective manufacture. To grip the small-scale specimens, a set of custom pull-rods that could be used within the environmental test chamber was also manufactured.

Figure 2: PE80 tensile specimens.

2.2 ODORANT GAS MIXTURES

Testing was performed in the presence of gas mixtures composed of each of the candidate odorants in hydrogen as listed below. The results were benchmarked against testing performed in air and in pure hydrogen.

NB (Cylinder 2376) – 1.49 ppm 2-methyl-2-propanethiol ((CH_3)$_3$CSH) and 0.42 ppm dimethyl sulphide ((CH_3)$_2$S) in hydrogen (H_2)

NB dilute (Cylinder NG814) – 1.31 ppm hexane (C_6H_{14}), 0.53 ppm 2-methyl-2-propanethiol ((CH_3)$_3$CSH) and 0.15 ppm dimethyl sulphide ((CH_3)$_2$S) in hydrogen (H_2)

THT (Cylinder A635) – 5.00 ppm tetrahydrothiophene (C_4H_8S) in hydrogen (H_2)

Acrylates (Cylinder NG802) – 1.12 ppm ethyl acrylate ($CH_2=CHCOOC_2H_5$), 0.70 ppm methyl acrylate ($CH_2=CHCOOCH_3$) and 0.05 ppm 2-ethyl-3-methylpyrazine ($C_7H_{10}N_2$) in hydrogen (H_2)

Norbornene (Cylinder A592) – 17.06 ppm 5-ethylidene-2-norbornene (C_9H_{12}) in hydrogen (H_2)

2.3 TEST PROCEDURE

SSRT of the PE80 polymer material was carried out according to BS EN ISO 22088-6:2009[6], which evaluates the susceptibility of a material to environmental stress cracking. The X42 pipeline steel was evaluated for susceptibility to environmentally assisted cracking using SSRT according to a modified version of ASTM G142[7]. The deviations from the standard were the geometry of the specimens and the strain rate, which had to be adapted to accommodate available equipment and material.

The general procedure involves subjecting test specimens to uniaxial tension at an increasing rate of strain until they either fracture or reach a pre-determined length. This is a severe ranking test that is designed to determine whether a material is susceptible to cracking in a given test environment. Polymer specimens are typically extremely ductile, and it is not necessary to strain them to complete failure. Instead, evaluation of polymer specimens is based on the development of crazes, which take up strain locally such that stress is reduced compared to an inert environment, and act as precursors to cracks. Figure 3 shows an example of a typical stress-strain curve in an inert environment compared to a reactive environment in which crazes have been induced. The method of determining the extent of craze formation, as described in the standard, requires the fitting of a third order polynomial to the stress-strain data up to the peak stress. The first derivative of stress with respect to strain for each test environment is then compared to that of the benchmark test performed in air. The stress at which the derivative falls to 75% of that measured in air is termed the departure stress:[6]

$$\frac{\left(\frac{d\sigma}{d\varepsilon}\right)_{env}}{\left(\frac{d\sigma}{d\varepsilon}\right)_{air}} = 0.75 \qquad (1)$$

where:
σ = stress
ε = strain

Metals are far less ductile and typically fracture within relatively modest amounts of extension. Evaluation is based on the ratio of plastic strain to failure determined for the material in the test environment to the corresponding value determined in the control environment, where the

plastic strain to failure is approximated to be the difference in crosshead displacement from the onset of specimen yielding to crosshead displacement at specimen fracture.[8]
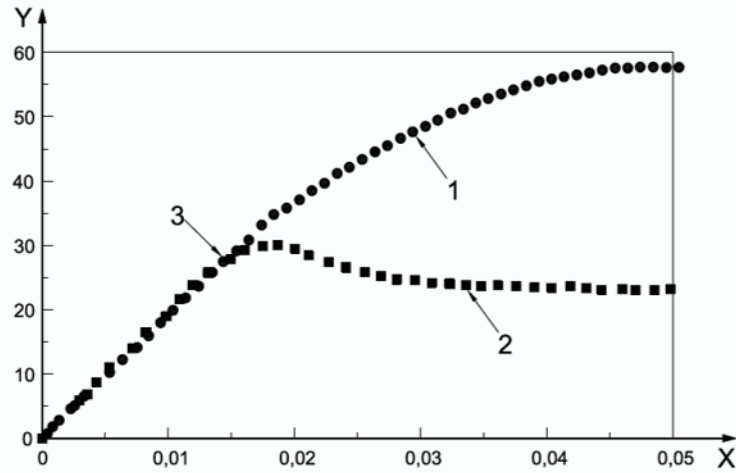

Figure 3: Typical stress (Y)-strain (X) plot showing difference in stress-strain profile for polymeric material exposed in an inert medium (1) and in a reactive test medium (2).[6] The departure stress is also indicated (3).

All tensile testing was performed on a calibrated Tinius Olsen H40K static tensile test machine at ambient temperature (22 ± 2 °C). The general test configuration is shown in Figure 1.

4
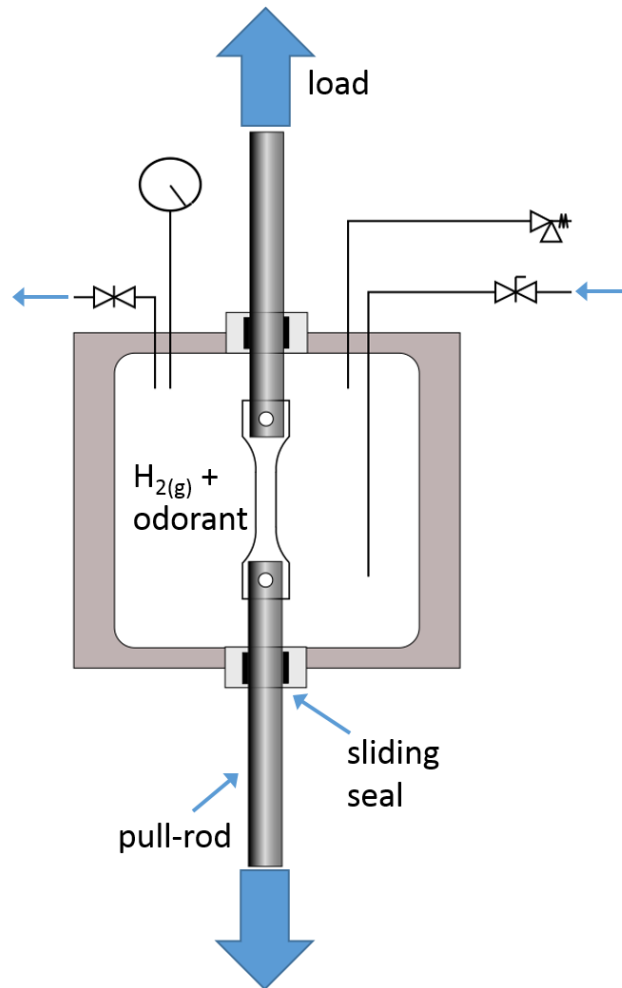
Figure 1: Configuration of test vessel for slow strain rate testing.

2.3.2 X42 steel

Tests on the X42 steel specimens were performed at 7 barg to simulate the maximum operating pressure within the intermediate pressure gas distribution network. Prior to testing, the high-pressure environmental chamber was deaerated by sweep-through purging using nitrogen gas at ambient pressure at a flow rate of 100 ml/min for 1 hour. The test gas was then introduced at ambient pressure at a flow rate of 100 ml/min for 1 hour to displace the nitrogen. Following this, the outlet was sealed, and the pressure was increased to 7 barg. The inlet was then sealed and SSRT was commenced at a strain rate of 8×10^{-6} s^{-1}. For metals, the susceptibility to environment assisted cracking in hydrogen is greater at lower strain rates. However, at very low strain rates, testing becomes impractical due to limitations in machine control and excessively long test times. In this study, a comparatively high strain rate of 8×10^{-6} s^{-1} was used, which was the slowest rate that could be achieved for small-sized specimens on the available equipment. The strain rate used was lower than that specified in ASTM G142[7] for smooth specimens and was within the 1×10^{-5} s^{-1} to 1×10^{-7} s^{-1} range specified in ASTM G129[8]. More conservative testing would evaluate the steel at a strain rate of 1×10^{-6} s^{-1} or lower. Specimens were extended until fracture, which marked the end of the test.

2.3.3 PE80 polymer

Given the use of small-scale specimens and the significantly lower tensile strength of the polymer specimens, it was decided to test the polymer at ambient pressure. This was done to avoid excessive measurement error associated with friction between the pull-rods and the

seals. By testing at ambient pressure, a seal against the pull-rods can be made with a silicone O-ring whose friction force is low relative to the ultimate tensile force sustained by the specimen. Prior to testing, the environmental chamber was deaerated by sweep-through purging using nitrogen gas at a flow rate of 100 ml/min for 1 hour. The test gas was then introduced at a flow rate of 100 ml/min for 1 hour to displace the nitrogen. Following this, the inlet and outlet to the vessel were sealed and the specimen was conditioned in the test environment for 24 hours before initiating SSRT. Specimens were then tested at a nominal strain rate of 9 x 10^{-6} s^{-1} as recommended in BS EN ISO 22088-6:2009.[6] The test was completed when specimens had been extended to 30 mm in length.

3. RESULTS

3.1 X42 STEEL

All the tests performed on X42 steel showed the same general trend with increasing applied strain. Stress increased linearly up to an upper yield point, after which there was an immediate drop in stress to a lower yield point. Beyond the lower yield point, stress increased up to the UTS, then decreased gradually until the specimen fractured. Plastic strain to failure was calculated as the change in strain between the upper yield point and specimen fracture. All of the steel specimens fractured within the gauge length at a total plastic strain in the range 0.57-0.61, with no secondary cracking. Figure 5 shows the stress-strain curve generated for a test performed in air and is representative of all the tests performed on X42 steel. From the figure, the steel displays double yielding, which is typical for this material. Each specimen exhibited necking prior to fracture (Figure 6) and revealed a fracture surface consistent with ductile failure. Figure7 shows a plot of the plastic strain to failure measured with duplicate specimens in each of the five candidate gas mixtures and the two benchmark environments. The plastic strain to failure observed in the presence of each of the candidate gas mixtures was comparable to that measured in air, indicating no measurable effect of either the hydrogen or the odorant on the steel under the conditions tested. For reference, the UTS measured in each of the tests is shown in Figure8.

For all tests performed on X42 steel specimens, the point of zero strain was taken at a preload of 300 N. This was done to mitigate the influence of the friction between the seals and the pull-rods, which varied between about 150 N and 250 N depending on the extent to which they were tightened. At 300 N, it was evident that friction had been overcome and a tensile load applied to the test specimen. The variability of the seal friction from one test to the next had only a small influence on the measured load and no influence on the measured plastic strain to failure.
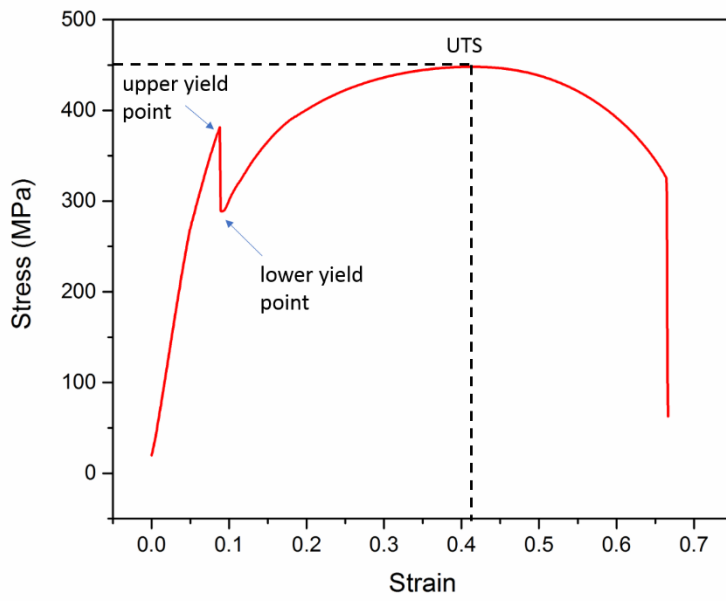
Figure 5: Example of the stress-strain behaviour of X42 steel in air; dashed lies indicate the UTS.

Figure 6: Typical example of a failed X42 steel tensile specimen.
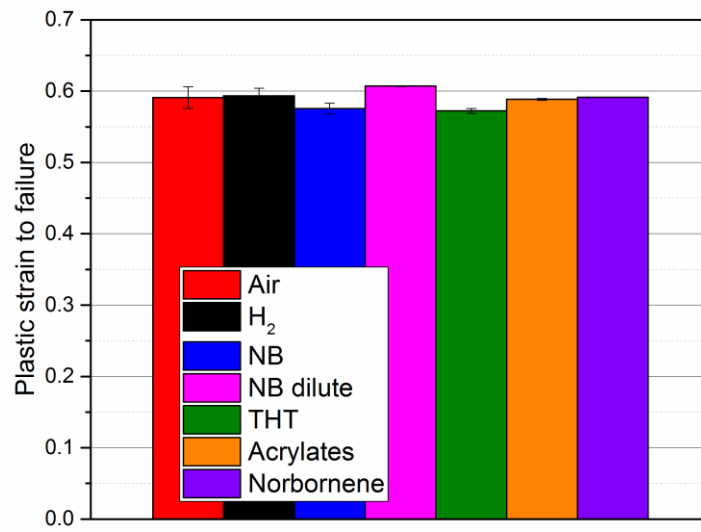
Figure 7: Plastic strain to failure of X42 steel in each test environment.
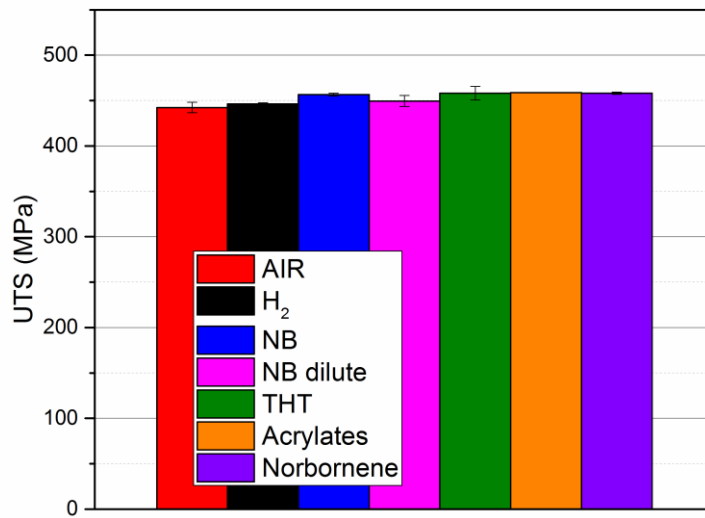

Figure 8: Ultimate tensile strength of X42 steel in each test environment.

3.2 PE80 POLYMER

Duplicate test specimens were extended to 30 mm (2.0 strain) without fracture in each environment, with the exception of the second test performed in pure hydrogen. In that test, there was slip between the specimen and grips and it was inadvertently released after reaching an applied strain of around 0.3. Stress vs. strain data for each test showed the same general trend, a rapid increase in stress with strain up to the ultimate tensile stress (UTS) at about 0.25-0.35 strain. Further extension resulted in a gradual loss of load bearing capacity up to the maximum strain of 2.0. An example of the full stress-strain behaviour of the polymer when tested in air is shown in Figure 9.

Compared with the benchmark tests performed in air, the influence of testing in each of the gas mixtures (including pure hydrogen) was a slight reduction in both the UTS and the apparent stiffness of the polymer (Figure 10 and Figure 11). The results did not give any indication that crazing had taken place, which is marked by a well-defined departure of the stress-strain curves measured in a test environment compared with that measured in inert environment (Figure). Instead, a gradual departure of the curves from the air data was observed from initial loading up to the UTS, which may be indicative of another process such as plasticisation. Figure 10 shows plots of stress vs. strain up to the UTS, with the magnitude of UTS for each test condition shown in Figure 11. The highest UTS was observed in air, where the measured value was 12.76 ± 0.01 MPa. The lowest value of UTS was 10.7 MPa, which was measured in the presence of the NB odorant gas mixture. Since no evidence of craze formation was observed in any of the tests, the departure stress could not be determined and is not reported.

Due to the relatively low load-bearing capacity of the polymer specimens, there was a concern that the signal to noise ratio of the load cell would be too low to resolve differences in material performance in the different environments. To address this concern, an in-house evaluation of the load cell was performed over the load range 0-120 N (corresponding to 0-13.3 MPa), which demonstrated that the cell could provide accurate measurements at low loads. For reference, a calibration curve of the load cell in the range of 0-120 N is provided in Appendix B.
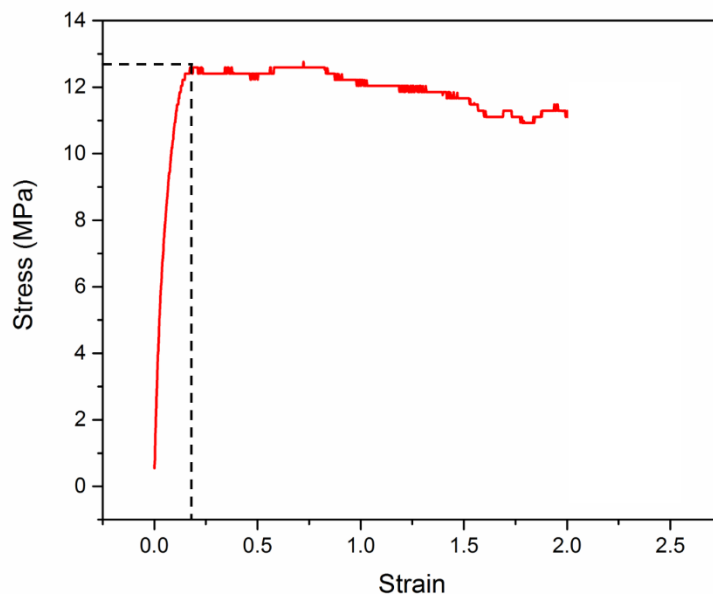

Figure 9: Example of the stress-strain behaviour of PE80 in air; dashed lies indicate the UTS.
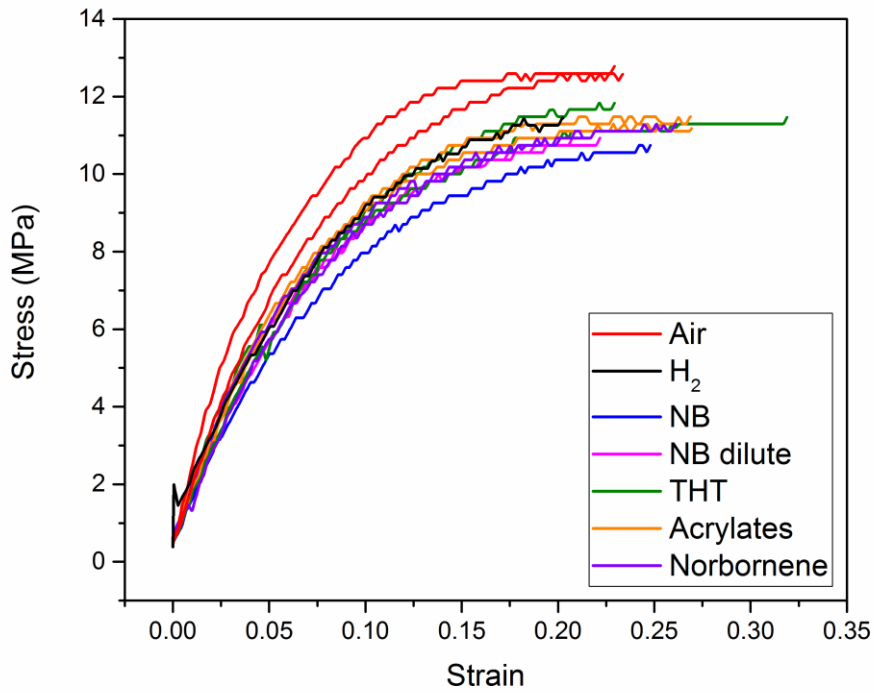
9

Figure 10: Duplicate plots of stress vs. strain for PE80 up to the UTS for each test environment (data from the repeat tests in pure hydrogen and odorant NB are omitted).
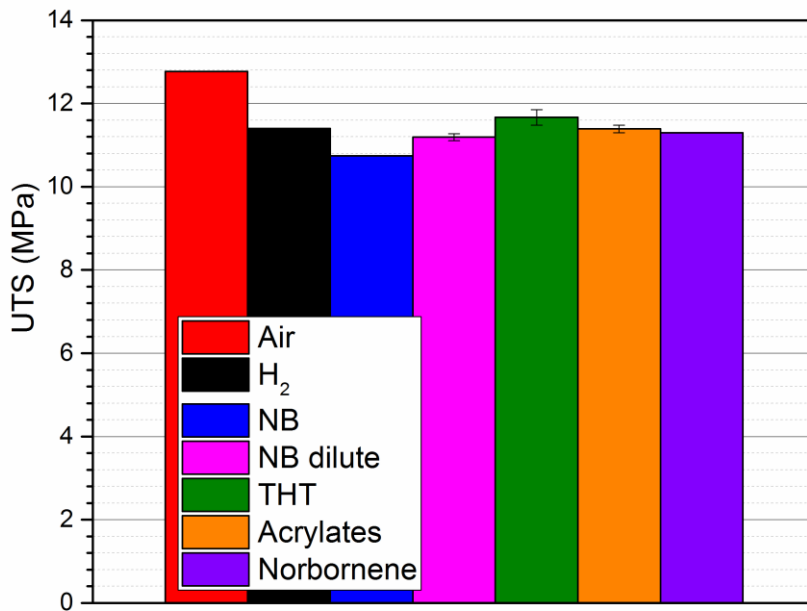

Figure 11: Plot of UTS for PE80 determined from duplicate tests in each of the test environments (only single results are plotted for pure hydrogen and odorant NB).

4. DISCUSSION

4.1 X42 STEEL

The results of tests on the X42 steel specimens indicate no discernible impact of any of the candidate odorants on the resistance to cracking of the steel when compared to its performance in air or pure hydrogen. The results of this preliminary investigation suggest that use of any of the candidate odorants in the presence of dry hydrogen at 7 barg pressure did not lead to environmentally assisted cracking of carbon steel, in the range of conditions tested. This is consistent with previous findings that have shown hydrogen embrittlement of carbon steel only at significantly higher partial pressures of hydrogen. For example, Figure 22 shows the dependence of tensile ductility on hydrogen partial pressure for SA 106 grade B carbon steel, which has a minimum UTS of 414 MPa[10], which is close to that of X42 (~450 MPa).
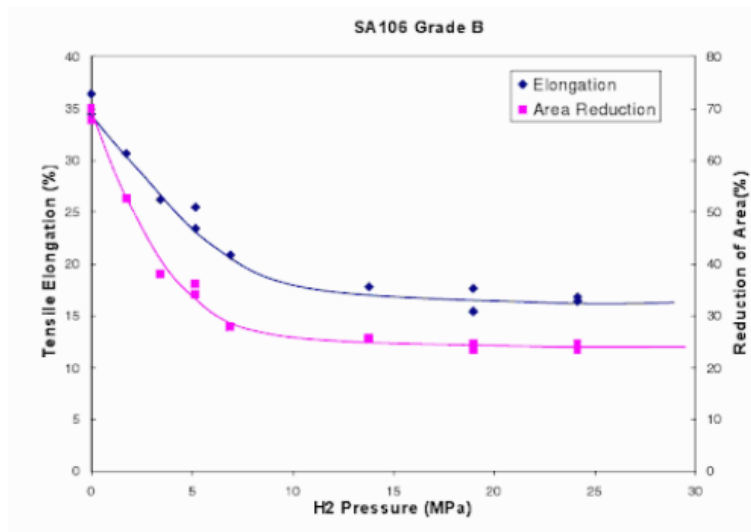
Figure 22: Dependence of tensile ductility on hydrogen pressure.[10]

Further work should be undertaken to assess the material in a wider range of possible operating conditions to give confidence that it has been evaluated under the most severe conditions that it might encounter in service. One factor that has not been considered here is the risk of water entering the gas distribution network, which would result in more severe conditions than a dry environment. In an aqueous environment, the presence of an odorant could render the solution corrosive, which in the presence of hydrogen could introduce a risk of stress corrosion cracking. Another point to consider is that these tests were performed at a comparatively high strain rate. It would be more conservative to use a strain rate closer to 1×10^{-7} s^{-1}, which would increase the time taken to complete an individual test and would require a tensile machine capable of finer control than that used in this work. Furthermore, owing to the low volumetric density of hydrogen compared to methane, there may be an economic incentive to run the network at pressures greater than 7 barg. In this case, it would be desirable to determine the threshold pressure that can be tolerated before hydrogen embrittlement becomes significant.

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4.2 PE80 POLYMER

The test results suggest that PE80 is not sensitive to environmental stress cracking under any of the conditions tested. This was demonstrated by the stress-strain data, which did not show any effect of crazing. Craze development is usually inferred by a rapid increase in strain at a given threshold stress, as shown in Figure 3. Although the plots shown in Figure showed no evidence of craze formation, all tests performed in the presence of hydrogen (either with or without odorant) showed a reduced UTS and a lower stiffness compared with tests performed in air. However, it should be noted that the precise stiffness of an individual specimen cannot be determined from stress vs. strain data as this is a measure of the stiffness of the entire load-train. In practice, the rest of the load-train is comparatively stiff compared to the polymer specimen. However, it is possible that the system contains some initial slack in the region of low-loading (0-120 N), where these tests were performed and for this reason the UTS is deemed a more reliable metric for comparison. The test performed in pure hydrogen gave a comparable result to the tests performed in the test gas mixtures and implies that the reduction in UTS is not related to the presence of odorant gas. A previous study found that long-term exposure of PE80 to hydrogen, at a pressure of 4 barg, had no effect on either the stiffness of the polymer or its elongation to failure[9], which suggests that the results were not attributable to exposure to hydrogen either. The reduction in UTS observed may instead be related to the difference in humidity between the test performed in air (~ 40% RH) and the tests performed with controlled gas mixtures (0% RH).

The stress-strain data from the duplicate test performed in the presence of odorant NB showed an unusual feature. Prior to reaching the UTS, there was a region of the stress vs. strain curve where the load was independent of strain (see Figure 33). This was followed by a further increase in stress and should not be confused with craze development, which would show a reduction in stress following the increase in strain. This feature is instead attributed to slip of the specimen within the grips used to transmit the load and should be considered a test artefact. For this reason, the results of this test were omitted from the calculation of UTS. Unlike steel specimens, polymer specimens cannot be held in place with a hole and pin configuration and instead rely on being held in place by the friction force administered by a set of grips. During the completion of these tests, it was discovered that occasional slip between the specimen and the grips could take place. This also occurred during the tests in hydrogen. In one test, slip occurred briefly at the beginning the test, but is not considered to have affected the overall determination of UTS as it caused only a small perturbation in load. Slip also took place during the second test and caused it to be released from the grips entirely. Release of the specimen occurred at a stress close to the UTS so the data were omitted from calculations. The full stress vs. strain curves from both tests are shown in Figure 44.

Overall, this initial investigation suggests that PE80 polymer is not susceptible to environmental stress cracking in the conditions tested.
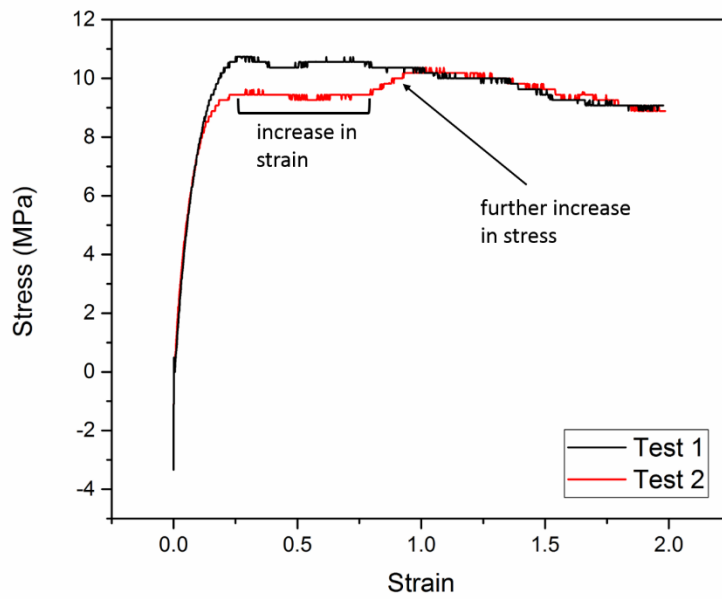
Figure 33: Duplicate plots of load vs. strain produced from SSRT of PE80 in the presence of odorant NB, showing an increase in strain associated with slip of the specimen grips.
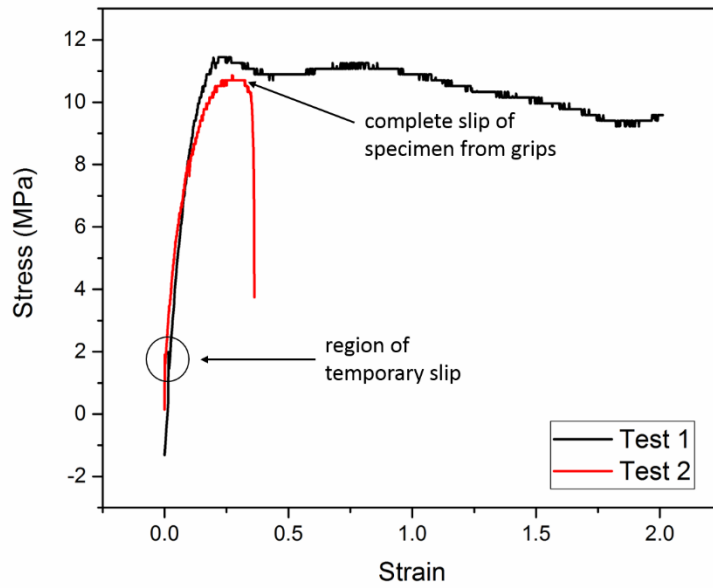

Figure 44: Duplicate plots of load vs. strain produced from SSRT of PE80 in the presence of pure hydrogen, showing a brief slip of each specimen in the grips at different stages of the test.

6. CONCLUSIONS

- X42 carbon steel was not susceptible to environmental stress cracking in pure hydrogen or in any of the candidate odorant gas mixtures under the conditions tested.

- PE80 polymer was not susceptible to environmental stress cracking in pure hydrogen or in any of the candidate odorant gas mixtures under the conditions tested.

- Further evaluation of both pipeline materials at their intended operation limits is recommended, with tests performed at lower strain rates and in higher partial pressures of hydrogen.

7. REFERENCES

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[2]   H.M. Government. The Clean Growth Strategy, 2017.
[3]   P.E. Dodds, W. McDowall, The future of the UK gas network, Energy Policy, 60, 305-316, 2013.
[4]   ISO 13734, Natural gas - organic components used as odorants - requirements and test methods, 2013.
[5]   S. Bartlett, A. Murugan, T. Bacquart, P. Brewer, Selection of Odorants for 100% Hydrogen Grid, NPL Report CMES 37, 2018.
[6]   Determination of resistance to environmental stress cracking (ESC), Part 6: Slow strain rate method (ISO 22088-6:2006), 2006.
[7]   ASTM standard G142-98, Standard test method for determination of suceptibility of metals to embrittlement in hydrogen containing environments at high pressure, high temperature, or both, ASTM International, West Conshohocken, PA, 2004.
[8]   ASTM standard G129-00, Standard practice for slow strain rate testing to evaluate the suceptability of metallic materials to environmetally assisted cracking, ASTM International, West Conshohocken, PA, 2000.
[9]   H. Iskov, Field test of hydrogen in the natural gas grid, EFP05 J.nr. 033001/33031-0053, DGC, 2010.
[10]   K. Xu, M. Rana, Tensile and fracture properties of carbon and low alloy steels in high pressure hydrogen, Proceedings of the 2008 International Hydrogen Conference, ASM International, 349-356, 2009.

Appendix A

Materials data sheet AJHH

Traceability ref 1120083617

Inšpekčný certifikát
Inspection certificate
EN 10204:2004/3.1

Číslo
Number **53444/1/2018**

List č. - *Sheet No.: 1 / 3*

Č.ext.obj. - External order No.:
011797

Číslo položky - Item number:
9

Č.obj.prij. - Consignee order No.:
3049/01000164

Číslo zákazky výrobcu - Manufacturer's works order number:
BA 201392/1/3   383A612

Číslo dopravného prostriedku - Transport No.:
RKR01928 RKRCX48

Číslo lodného listu - Loading Bill No.:
35824

Číslo avíza - Dispatch note:
3826667

Výrobok - Product:

Rúry oceľové bezošvé, valcované za tepla - rúry pre potrubia pre horľavé médiá
Seamless hot finished steel tubes - pipelines for combustible fluids

Vonkajší priemer - Outside diameter:	88.900 mm
Hrúbka steny - Wall thickness:	11.130 mm
Dĺžka - Length:	6000.000 mm [-0 +100] mm
Počet kusov - Number of pieces:	16
Celková dĺžka - Total length:	96.00 m
Celková hmotnosť - Total mass:	2083.00 kg

Materiál - *Material*:

B PSL1 API SPEC. 5L Ed.45th2012 Err.2015,   Grade B ASME SA-106/SA-106M Ed.2017,
Grade B ASME SA-53/SA-53M Ed.2017,   Grade B ASTM A 106/A 106M -15,   Grade B ASTM A 53/A 53M -12,
P265TR2 EN 10216-1 :2013,   X42 PSL1 API SPEC. 5L Ed.45th2012 Err.2015

Trieda - *Class*: 1

Stav dodania - *Products as delivered condition*:

Normalizačné tvárnenie - *Normalizing forming*

Technické predpisy - *Technical requirements/Demand*:

API SPEC. 5L Ed.45th2012 Err.2015,   ASME SA-106/SA-106M Ed.2017,   ASME SA-53/SA-53M Ed.2017,
ASME SA-530/SA-530M Ed.2017,   ASTM A 106/A 106M -15,   ASTM A 53/A 53M -12,   ASTM A 530/A 530M -12,
EN 10216-1 :2013,   PED 2014/68/EU

Číslo tavby Cast number	Počet kusov Number of pieces	Dĺžka Length [m]	Hmotnosť Mass [kg]	Druh tavenia Steelmaking process
84245	16	96	2083	E

E = elektrická oblúková pec - *electric arc furnace*

Druh ocele - *Steel grade*:

úplne ukľudnená oceľ - *fully killed steel*

Miesto v Podbrezovej *Location* amb	Dátum 09.10.2018 *Date*	Záverečný znalec *Works Inspector*	Ing. Vojtas Miroslav

15

ŽELEZIARNE° PODBREZOVA

Inšpekčný certifikát
Inspection certificate
EN 10204:2004/3.1

Číslo
Number

53444/1/2018

List č. - *Sheet No.: 2 / 3*

Úprava povrchu - *Surface protection:*

Ochrana povrchu UV lakom - *Surface protection with UV lacquer*

Chemické zloženie - *Chemical composition:*

Číslo tavby Cast number		C [%]	Mn [%]	Si [%]	P [%]	S [%]	Cu [%]	Cr [%]	Ni [%]	Al [%]	Mo [%]	Ti [%]	V [%]	Nb [%]
	Predpis - *Requirement*													
	min.			0.10						0.020				
	max.	0.20	1.06	0.40	0.025	0.010	0.30	0.30	0.30		0.08	0.040	0.020	0.010
84245		0.15	0.52	0.23	0.013	0.007	0.17	0.07	0.08	0.022	0.01	0.001	0.007	0.001

Číslo tavby Cast number		B [%]	Exp.1 [%]	Exp.2 [%]	Esp.3 [%]
	min.				
	max.	0.0010	0.41	0.150	0.060
84245		<0.0001	0.27	0.009	0.008

Esp.1 = CEV = $C + Mn/6 + (V+Mo+Cr)/5 + (Ni+Cu)/15$

Esp.2 = $V + Nb + Ti$

Esp.3 = $V + Nb$

Výrobková analýza - *Product analysis:*

Číslo tavby Cast number		C [%]	Mn [%]	Si [%]	P [%]	S [%]	Cu [%]	Cr [%]	Ni [%]	Al [%]	Mo [%]	Ti [%]	V [%]	Nb [%]
84245	1	0.15	0.53	0.23	0.013	0.007	0.17	0.07	0.08	0.022	0.02	0.002	0.007	0.001
84245	2	0.15	0.53	0.23	0.013	0.006	0.17	0.07	0.08	0.023	0.02	0.002	0.007	0.001

Číslo tavby Cast number		B [%]
84245	1	<0.0003
84245	2	<0.0003

Skúška ťahom - *Tensile test :*   20 °C

	Číslo tavby Cast number	Vzorka č. Test No.	Rozmery Dimensions [mm]	Smer odberu vzorky Direction of the test piece	Medza klzu Yield point - Proof stress		Pevnosť v ťahu Tensile strength	Ťažnosť Elongation	
					RcH [MPa]	R|0,5 [MPa]	Rm [MPa]	A5,65 [%]	2" [%]
C. Nr			Predpis - *Requirement:*	min. max.	265 ...	290 ...	415 570	21.0 ...	* ...
1	84245	A042472/18	14.65x11.35	L	329	330	452	31.7	37.6

* Ťažnosť - *Elongation* : min. $(1940 \cdot So^{**}0.2)(Rm^{**}0.9)$

Skúška nárazom v ohybe Charpy - *Charpy impact test:*

C. Nr	Číslo tavby Cast number	Vzorka č. Test No.	Predpis Requirements min-max. [J]	Jednotlivé hodnoty Individual values [J]	Priemerná hodnota Mean value [J]	Teplota skúšania Test temperature [st']
1	84245	A042471/18	KV 40 - ---	208, 209, 210	209	0

Miesto v Podbrezovej
Location   amb

Dátum 09.10.2018
Date

Závodný znalec
Works Inspector

Ing. Vojtas Miroslav

ŽELEZIARNE PODBREZOVA

ŽELEZIARNE° PODBREZOVA

Inšpekčný certifikát
Inspection certificate
EN 10204:2004/3.1

Číslo
Number

53444/1/2018

List č. - *Sheet No.*: 3 / 3

Č. Nr	Vzorka č. Test No.	Rozmery Dimensions [mm]	Smer odberu vzorky Direction of the test piece
1	A042471/18	10.00x10.00	L

Skúška stlačením vyhovela.
Flattening test without objections.

Skúška vodným tlakom vyhovela.   API 5 L 20.50 MPa 5 sec 100%
Hydraulic pressure test without objections.

Skúška vírivými prúdmi vyhovela.   ASME SA - 106/E309   100 %   Priemer vývrtu: 2.20 mm
Eddy current test without objections   *Drilled hole:*

Skúška vírivými prúdmi vyhovela.   ASTM A106/E309   100 %   Priemer vývrtu: 2.20 mm
Eddy current test without objections   *Drilled hole:*

NACE MR 0175/ISO 15156-2 Ann.A2.1.2 and A2.1.3 and NACE MR 0103 par.2.1

Systém kvality výrobcu je certifikovaný fy SGS podľa ISO 9001, číslo certifikátu HU95/462K, platnosť certifikátu je do 18.7.2020.
Producer's Quality Assurance System is certified according to ISO 9001 by SGS, certificate no. HU95/462K, validity: 18.7.2020.

Systém kvality výrobcu bol podrobený špecifickému hodnoteniu pre materiály (Článok 4.3 a 7.5, Príloha I Smernice PED 2014/68/EU). Certifikát 07/202/9150/WZ/0915/17 vydalo notifikované miesto 0045 TÜV NORD Systems GmbH s platnosťou do 03/2020. Rozsah platnosti certifikátu zahŕňa predmetné výrobky.
The producer has a specific reviewed quality system for materials according to the Article 4.3 and 7.5, Annex I of the Directive PED 2014-68/EU. The certificate 07/202/9150/WZ/0915/17 with the validity till 03/2020 was issued by the Notified Body TÜV NORD Systems GmbH, Code 0045. The mentioned products belong to the certificate validity range.

Všetky výrobky vyhovujú vyššie uvedeným normám a požiadavkám v objednávke.
All products meet requirements of above mentioned standards and requirements specified in the order.

Vizuálna kontrola a rozmery vyhoveli (100 %).
Visual inspection and dimensional check without objections (100 %).

Miesto v Podbrezovej   Dátum 09.10.2018   Závodný znalec   Ing. Vojtas Miroslav
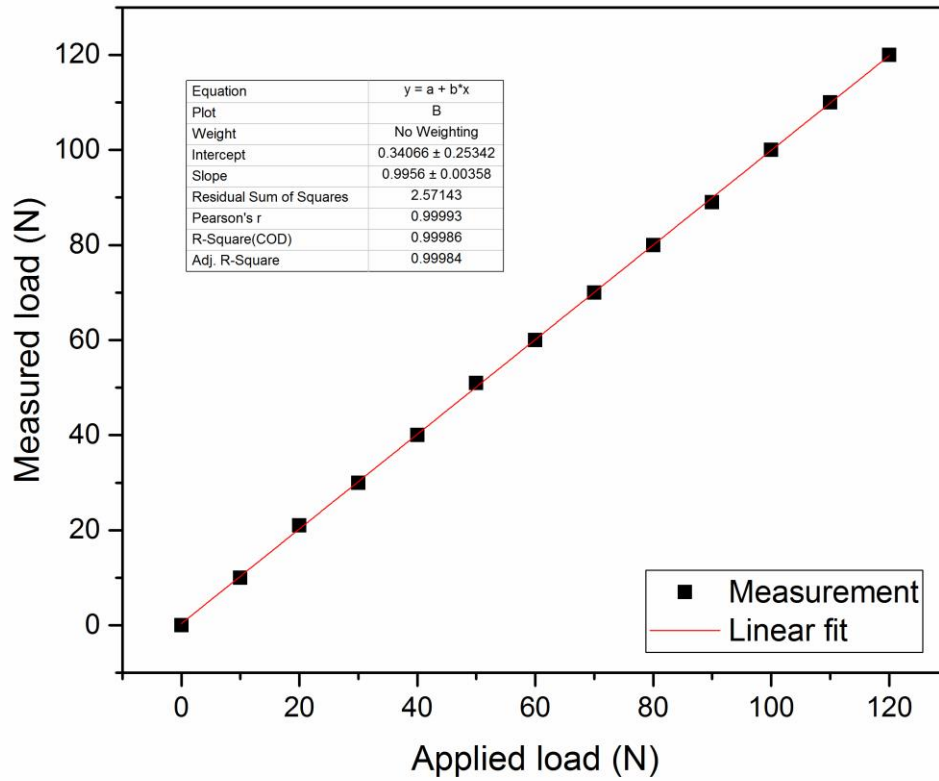*Location*   *Date*   *Works Inspector*

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Appendix B

LOAD CELL CALIBRATION CURVE

Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	0.34066 ± 0.25342
Slope	0.9956 ± 0.00358
Residual Sum of Squares	2.57143
Pearson's r	0.99993
R-Square(COD)	0.99986
Adj. R-Square	0.99984

NPL REPORT EMES (RES) 085

INFLUENCE OF HYDROGEN ODORANT CHEMISTRY ON FLAME BOILER CORROSION

JAMES HESKETH

NPLML - COMMERCIAL

APRIL 2019

INFLUENCE OF HYDROGEN ODORANT CHEMISTRY ON FLAME BOILER CORROSION

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CONTENTS

1   INTRODUCTION

The UK government is committed to reducing greenhouse gas emissions; by 2050 we must have reduced these emissions by 80% from the 1990 levels.[1] As highlighted in the UK's Clean Growth Strategy, the low carbon economy in the UK could grow by 11% between 2015 and 2030.[2] The UK gas infrastructure currently supplies natural gas to homes and industry; we are already reducing carbon emissions by introducing biomethane into the mix. With 90% of grid pipelines being replaced by polyethylene by 2032[3] and new technologies becoming available for efficient and renewable hydrogen production, a 100% hydrogen gas grid is certainly possible and would contribute significantly towards meeting the UK 2050 target. Before we can establish whether a scenario such as the 100% hydrogen grid would be possible, work is required to understand various implications, including safety.

Natural gas contains an odorant that can be detected via the human olfactory system at less than 20% of the gas's lower flammability limit.[4] This sensitive system quickly alerts any user to a leak of natural gas; it is simple but effective. Hydrogen is an odourless, hazardous material that has a wide flammability window (4 – 74%) and can permeate through tiny leaks. Hydrogen production methods (commonly steam methane reforming or electrolysis) do not, as part of the process, introduce controlled amounts of odorant into the gas, and therefore an odorant would need to be added downstream. It is possible that current odorants used within the natural gas grid may be suitable in a 100% hydrogen grid, however extensive testing needs to be performed beforehand as, for example, the odorant may not behave the same way in hydrogen compared to natural gas.

As part of the SGN funded Hydrogen 100: Hydrogen Odorants and Leak Detection project, NPL performed a review of relevant standards and regulations in order to provide a suitability criteria for an odorant that could be used within the UK's 100% hydrogen grid.[5] This yielded a recommendation of five potential candidates, as chosen by SGN, to be evaluated by the following criteria.
- Olfactory characterisation
- Fuel cell degradation
- Pipeline corrosion (both metal and plastic piping)
- Boiler corrosion
- Stability
- Health and environmental effects

This report details the testing procedure used to evaluate the five candidate odorants based on their tendency to cause boiler corrosion by formation of an acidic condensate when combusted in the presence of hydrogen.

2   THEORY

DETERMINATION OF CONDENSATE CHEMISTRY

The chemistry of the condensate produced from the combustion of each of the five candidate odorants, in its relevant stoichiometric ratio with hydrogen, was calculated for conditions simulating those encountered in a flame boiler system. Calculations were performed by Hampton Thermodynamics using MTData Version 6.0 and are detailed in a separate report.[6] A significant assumption of the modelling was that combustion was controlled to prevent the formation of NO_X. Discussion with Worchester Bosch confirmed that this was a valid assumption for the typical operating conditions of flame boilers. When NO_X compounds are allowed to form, the resulting condensate chemistry is dominated by the formation of nitric acid and the influence of the presence of any odorant is negligible. Hence, for each candidate odorant, the condensate chemistry that formed included carbonic acid due to the small amount of CO_2 produced from the combustion of the odorant. Odorants that contained sulphur produced condensates that also contained sulphuric acid.[6] To provide a benchmark set of conditions, the condensate produced during the combustion of a mixture of methane and tertiary butyl mercaptan + dimethyl sulphide was also evaluated. The chemistry and concentration of each candidate odorant plus the benchmark condition are detailed below:

A) Cylinder 2376 – 1.49 ppm 2-methyl-2-propanethiol $((CH_3)_3CSH)$ and 0.42 ppm Dimethyl sulphide $((CH_3)_2S)$ in Hydrogen (H_2)

B) Cylinder NG814 – 1.31 ppm Hexane (C_6H_{14}), 0.53 ppm 2-methyl-2-propanethiol $((CH_3)_3CSH)$ and 0.15 ppm Dimethyl sulphide $((CH_3)_2S)$ in Hydrogen (H_2)

C) Cylinder A635 – 5.00 ppm Tetrahydrothiophene (C_4H_8S) in Hydrogen (H_2)

D) Cylinder NG802 – 1.12 ppm Ethyl acrylate $(CH_2=CHCOOC_2H_5)$, 0.70 ppm Methyl acrylate $(CH_2=CHCOOCH_3)$ and 0.05 ppm 2-ethyl-3-methylpyrazine $(C_7H_{10}N_2)$ in Hydrogen (H_2)

E) Cylinder A592 – 17.06 ppm 5-ethylidene-2-norbornene (C_9H_{12}) in Hydrogen (H_2)

F) Benchmark – 1.5 ppm Tertiary butyl mercaptan $(C4H10S)$, 0.4 ppm Dimethyl sulphide $((CH_3)_2S)$ in Methane (CH_4)

For the sulphur containing odorants, the condensate chemistry is heavily influenced by temperature. At the point condensation starts to form (T_{cond}), the chemistry of the solution is that of concentrated sulphuric acid.[6] As the temperature is reduced, a greater amount of water enters the condensate diluting it and raising the pH. Hence, to allow a meaningful comparison of the condensates with regard to boiler corrosion, the resulting chemistry was calculated at the temperature at which 10% condensation occurs $(T_{10\%})$ as shown in Table 1.

Table 1: Temperature and pH of condensate 10% condensation[6].

Odorant	T_{cond} / °C	$pH(T_{cond})$	$T_{10\%}$ / °C	$pH(T_{10\%})$
A	117	-2.5	61	2.8
B	111	-2.5	61	3.1
C	124	-2.6	61	2.4
D	62	6.4	61	6.5
E	62	6.2	61	6.2
F	106	-2.6	53	2.9

3   METHODOLOGY

TEST SPECIMENS

Aluminium test specimens were prepared from samples of a flame boiler heat exchanger by Worcester Bosch. Samples were taken from three different components, labelled WB5, WB6, and WB7, giving specimens with a range of surface finish and geometry as shown in Figure 1.

Figure 1: Photograph showing the three types of test specimen.

CONDENSATE CHEMISTRY

Test environments consisted of aqueous solutions prepared to simulate the calculated condensate chemistry at the point at which 10% condensation had occurred. For the sulphur containing odorants A (2-methyl-2-propanethiol + Dimethyl sulphide), B (2-methyl-2-propanethiol + Dimethyl sulphide) and C (Tetrahydrothiophene), and the benchmark condition F, this consisted of reagent grade sulphuric acid diluted with deionised water to give the same pH as shown in Table 1. The pH was adjusted at room temperature and heated to the test temperature, which causes a slight discrepancy between the test conditions and the modelled pH. This error was calculated using MTData Studio 6.0 and found to be less than 0.05 pH units for each of the test conditions, which is not considered significant.

Table 1 shows the pH arising from the combustion of the two non-sulphur containing odorants D (Ethyl acrylate + Methyl acrylate + 2-ethyl-3-methylpyrazine) and E (5-ethylidene-2-norbornene) at 10% condensation. The calculated value of pH only considers CO_2 arising from the combustion of each odorant in hydrogen and does not include the influence of the CO_2 already present in air, which for these conditions is the dominant species influencing pH. The partial pressure of CO_2 in air at 1 bar is 40 Pa, whereas the additional CO_2 produced by the combustion of each odorant is just 0.2 Pa for odorant D and 3.6 Pa for odorant E. To simulate these conditions, the condensate for odorant D was taken as deionised water exposed to air at atmospheric pressure. For odorant E, the test vessel was sealed from the atmosphere and a small volume of pure CO_2 was added to the volume of gas in the test vessel to increase the CO_2 partial pressure from 40 Pa to 44 Pa.

Table 2: Test conditions

Odorant	Condensate	$T_{10\%}$ / °C	$pH(T_{10\%})$
A	Sulphuric acid	61	2.8
B	Sulphuric acid	61	3.1
C	Sulphuric acid	61	2.4
D	Deionised water + air	61	6.5 (5.74 in air)
E	Deionised water + air + CO_2	61	6.2 (5.72 in air)
F	Sulphuric acid	53	2.9

TEST CONFIGURATION

Specimens of each type were stamped with a number from 1 to 6 for identification purposes and were photographed. Before testing, they were placed in acetone in an ultrasonic bath for 10 minutes to degrease the surface and remove any loose particles, then rinsed in propanol and dried in air. The mass of each specimen was measured on a calibrated mass balance accurate to 0.1 mg, and recorded. One of each type of specimen was then placed in a culture vessel containing a solution of one of the 6 calculated condensate chemistries as indicated in Table 2. The solution was heated to the relevant temperature, and maintained to within ±0.5 °C for 1 month. To ensure a uniform temperature profile within the vessels, they were all agitated using magnetic stirrer bar rotating at 300 rpm. After 1 month, the specimens were removed from the test solutions. Where necessary, specimens were abraded with a plastic brush to remove loosely adhered corrosion product. They were then chemically cleaned in concentrated nitric acid for 5 minutes as described in ASTM G1[7] and the mass was re-measured and recorded. An image of the test configuration is presented in Figure 2.

Figure 2: Test configuration.

4   RESULTS

Images of the test specimens taken before and after testing are presented in Figure 3 to 8. Specimens tested in the condensates that contained sulphur (A, B, C and F) all exhibited heavy pitting corrosion, visible to the naked eye. Specimens tested in the condensates of candidate odorants D and E presented no evidence of corrosion when viewed using optical microscopy to a magnification of ×10.

The extent of corrosion was evaluated by the % change in mass of each specimen as shown in Figure 9 to 11. It is typical to quote corrosion mass loss normalised by surface area to give a rate of corrosion penetration. However, that is not suitable in this situation since specimens exhibited localised pitting rather than general uniform corrosion. In addition, the test specimens comprised highly irregular boiler components with rough surfaces, whose surface area is difficult to establish with accuracy.

Figure 9 - 11 show that in the condensates formed from odorants D and E there was little or no mass loss from the test specimens, and in some cases specimens appeared to have gained mass – possibly due to growth of the oxide/hydroxide layer. Of the candidate odorants containing sulphur (A, B and C), B was the least corrosive and C was the most corrosive. When comparing the results against the benchmark condensate (F), the condensates of odorants B, D and E were consistently less corrosive.

Figure 3: Pre-test images of the WB5 specimens tested in condensate A to F (left to right, top to bottom).
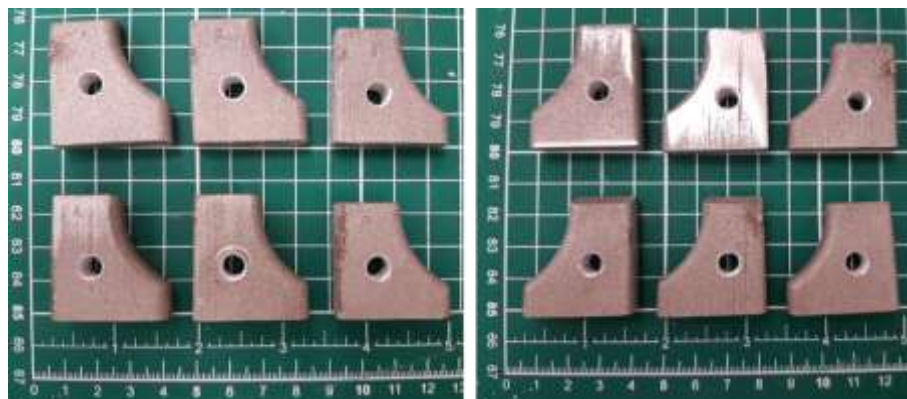
Figure 4: Pre-test images of the WB6 specimens tested in condensate A to F (left to right, top to bottom).
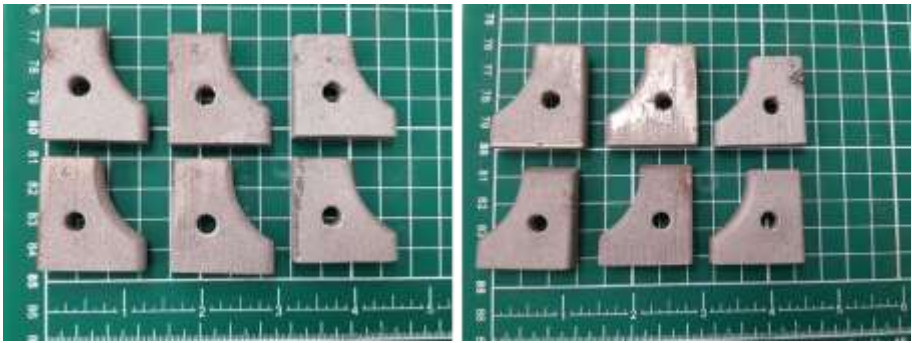
Figure 5: Pre-test images of the WB7 specimens tested in condensate A to F (left to right, top to bottom).
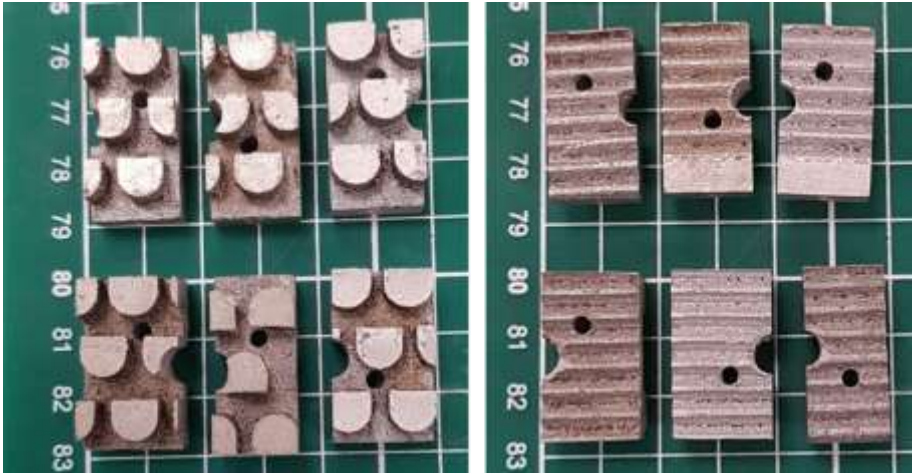
Figure 6: Post-test images of the WB5 specimens tested in condensate A to F (left to right, top to bottom).
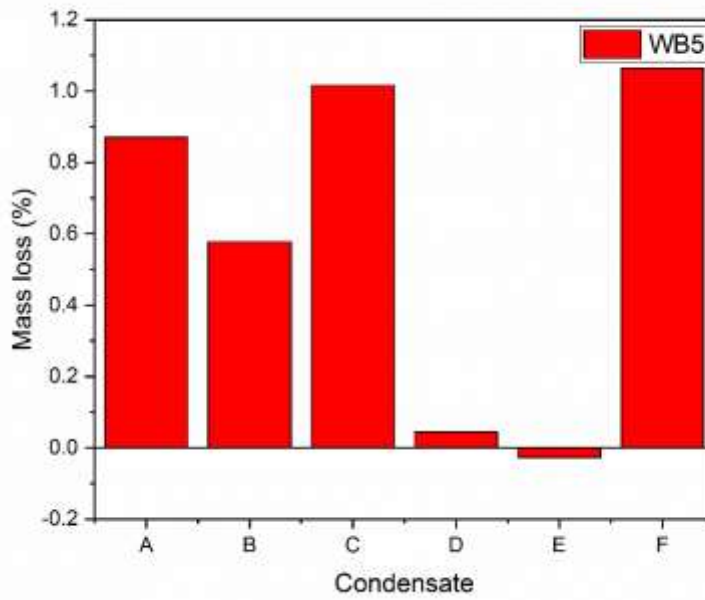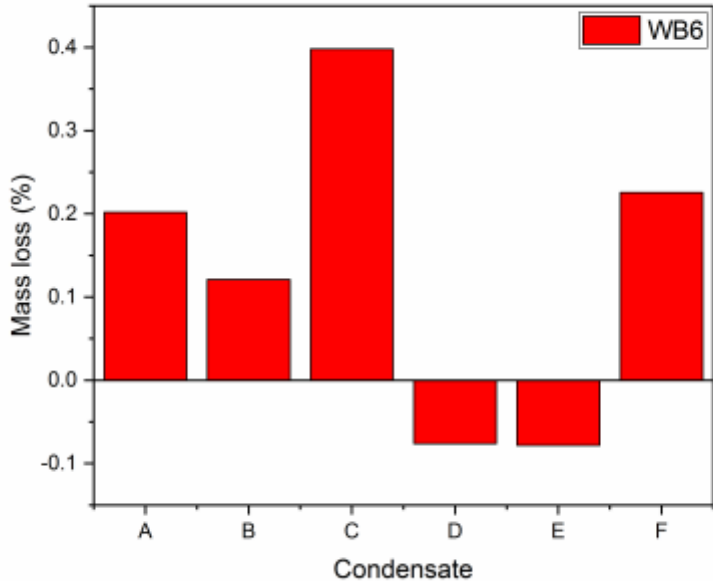

Figure 7: Post-test images of the WB6 specimens tested in condensate A to F (left to right, top to bottom).

Figure 8: Post-test images of the WB7 specimens tested in condensate A to F (left to right, top to bottom).

Figure 9: Percentage mass loss of the WB5 specimens.

Figure 10: Percentage mass loss of the WB6 specimens.
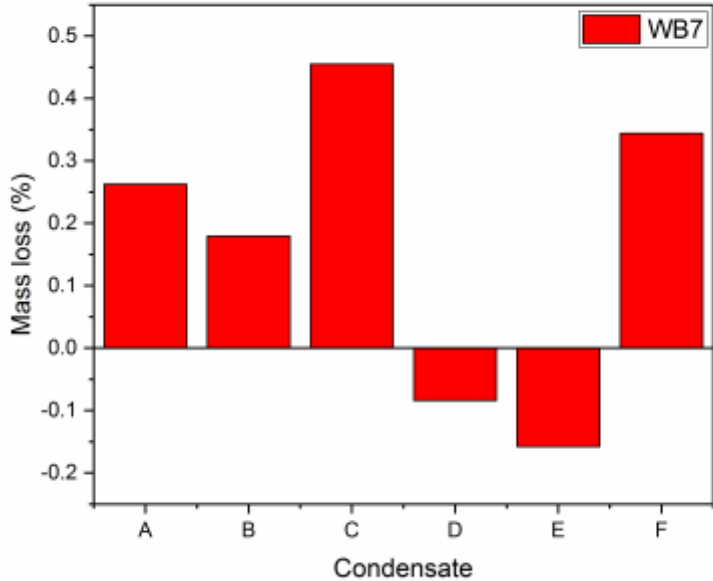
Figure 11: Percentage mass loss of the WB7 specimens.

5 DISCUSSION

The results of the mass loss tests were as to be expected. Condensates formed from odorants D and E did not result in corrosion of the aluminium test specimens since they were essentially deionised water and the aluminium remained passive. Comparing odorants A, B and C, the more acidic the condensate the greater the mass loss due to an increasing severity of pitting corrosion. This is explained by the effect of pH on the stability of the protective passive film, which becomes less stable in more acidic conditions.

There is no obvious reason why the benchmark condensate appeared to be as corrosive as the condensate of odorant A and odorant C, given that it was less acidic and heated to a lower temperature (53°C compared to 61°C). However, a likely explanation for this is that the specimens were non-uniform and had inhomogeneous surfaces. It was observed that pitting corrosion tended to initiate at specific locations on the test specimens and was influenced by their individual surface morphology. An example of which is shown in Figure 12, and demonstrates that one of the surfaces of the WB6 specimens was more susceptible to pitting corrosion due to it having a machined surface. This is expected to increase variability between the results and is compounded by the fact that pitting corrosion is an inherently stochastic process. Hence, in more acidic conditions where pitting corrosion is considerable, variation in the specimen's surface finish/preparation has a greater impact on the extent of pitting than small changes in the solution pH. This is important for predicting the impact of condensate chemistry on the corrosion of boiler components in-service, which will inherently exhibit large variability in surface state/condition.

It must also be considered that the conditions tested in this study reflect the anticipated condensate chemistry that forms at 10% condensation. The actual chemistry that the boiler experiences in service will be heavily influenced by the temperature. For sulphur containing odorants, at lower temperatures the condensate will be less acidic and hence less corrosive, but at higher temperatures the condensate will approach that of concentrated sulphuric acid. In very acidic conditions (pH > 0), the relationship between the corrosivity of the solution and the pH is more complex and the most severe conditions may not occur at the lowest pH. Table 3 shows the ranking of the corrosivity of the condensates of the five candidate odorants, based on the extent of corrosion of the different aluminium specimens. A comparison against the benchmark condensate was only given if it was consistent across all three specimen types.

This study provided preliminary investigation into the influence of condensate chemistry on flame boiler corrosion, and only provides a ranking of the odorants in one hypothetical operating condition. As highlighted in a previous report[5], the chemistry of a condensate varies considerably over a fairly small temperature range. With this in mind, a more exhaustive study into the corrosivity of the most suitable condensates over a range of typical operating conditions would give added confidence that they can be used within existing flame boilers, without compromising their operating life due to corrosion.

Figure 12: Photograph of WB6 specimens tested in condensate A to E (left to right), showing preferential pitting corrosion of the machined face.

Table 3: Ranking of the relative corrosivity of the condensates from 1 – most corrosive to 5 – least corrosive.

	A	B	C	D	E
WB5	2	3	1	4	5
WB6	2	3	1	4=	4=
WB7	2	3	1	4=	4=
Overall rank	2	3	1	4=	4=
Comparison to benchmark	Inconclusive	Less corrosive	Inconclusive	Less corrosive	Less corrosive

6   CONCLUSIONS

- Complete combustion of hydrogen in the presence of odorants that are sulphur-free is not anticipated to produce a condensate that is corrosive towards aluminium boiler components at temperatures where 10% or more of the combustion products have condensed.

- Condensates of odorants containing sulphur are substantially more corrosive than those that are sulphur-free, owing to the formation of sulphuric acid.

- The corrosivity of condensates produced from sulphur containing odorants (A, B and C) can be ranked according to their pH, where the more acidic condensates are more corrosive towards aluminium in the pH range 2.4-3.1.

- When the condensates formed from the combustion of hydrogen and the sulphur-free odorants were compared to the benchmark condensate (produced from the combustion of methane with tertiary butyl mercaptan and dimethyl sulphide), it showed them to be considerably less corrosive.

- Comparison of the condensates A and C with the benchmark condensate showed no statistically significant difference in their corrosivity. This is ascribed to the variability of the surface finish of the test specimens, which influences the susceptibility towards pitting corrosion.

- Odorants B, D and E appear to be the most suitable candidates as they produce condensates that are less corrosive when compared to the benchmark condensate. Consequently, their use in flame boilers is not anticipated to have an adverse effect on operating life due to corrosion.

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NPL REPORT EET (RES) 004

PRELIMINARY SCREENING OF CANDIDATE ODORANTS FOR THE HYDROGEN GAS GRID: IMPACT ON FUEL CELL PERFORMANCE

HANS BECKER AND GARETH HINDS

NPLML - COMMERCIAL

JULY 2019

Preliminary screening of candidate odorants for the hydrogen gas grid: impact on fuel cell performance

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Electrochemistry Group

EXECUTIVE SUMMARY

Preliminary screening of five different candidate odorants for use in a potential future hydrogen gas grid was carried out to assess their compatibility with polymer electrolyte membrane (PEM) fuel cell operation. Evaluation of the odorants was carried out via single-cell fuel cell testing to determine their short term effect on the cell voltage during constant current operation at 0.8 A cm^{-2}. The three sulfur-containing odorant gas mixtures (NB, THT and NB dilute) led to a significant and largely irreversible decrease in cell voltage over a 4 hour period, demonstrating that they are incompatible with PEM fuel cell operation. In contrast, the rate of cell voltage decay for the non sulfur-containing odorant gas mixtures (norbornene and acrylates) was within the range observed in pure hydrogen during the 1 h baseline period, making it difficult to determine conclusively that there is no detrimental effect of their presence. A significantly longer test duration for both the baseline tests in pure hydrogen and the odorant exposure tests is recommended to provide more conclusive qualification of these odorants.

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CONTENTS

1   INTRODUCTION

The UK has committed to reduce its greenhouse gas emissions by 80% from 1990 levels by 2050. Through the Clean Growth Strategy and The Road to Zero policy, significant measures have been proposed by the UK government, such as the ban on selling new petrol and diesel vehicles by 2040[1]. Fuel cell electric vehicles (FCEVs) are promising candidates to replace petrol and diesel vehicles due to their rapid refuelling time (~ 5 minutes) and relatively high range (~ 300 miles), while their high specific energy density is particularly favourable for heavy goods vehicles[1]. Sustainable use of FCEVs requires hydrogen that can be sourced from electrolysis coupled with electricity from renewable technologies such as solar and wind power. However, the main barrier to hydrogen-powered transport is the lack of a hydrogen refuelling infrastructure.

In parallel, gas network operators have started to investigate the possibility of reducing their carbon footprint by making the transition from methane to hydrogen. This could be either through blending of hydrogen within the existing grid or by moving to 100% hydrogen. In addition to supplying hydrogen for combustion in domestic and industrial applications, a hydrogen gas grid would provide a convenient means of distributing hydrogen for transport applications. However, one potential drawback is that the performance of polymer electrolyte membrane (PEM) fuel cells is very sensitive to trace levels of contaminants in hydrogen, particularly those containing sulfur originating from the steam methane reforming process.[2]

Like methane, hydrogen is an odourless and colourless gas with a relatively wide flammability range (4 - 75%), making it potentially dangerous in the case of leaks. In the existing gas grid, odorants are injected into the methane for safety reasons, in order to stimulate the human olfactory system by triggering a characteristic smell. According to the Gas Safety (Management) Regulation 1996, an olfactory degree of 2 should generally be achieved at 20% of the lower flammability limit (LFL) of the gas, corresponding to 1% mixture of natural gas in air[3]. Odorants also need to satisfy other criteria including[4]:

- Chemical stability
- High vapour pressure
- Non-corrosivity
- Low tendency for adsorption in soil
- Odorant smell must not be masked by other hydrocarbons
- Odorant must not contain water

The 100% Hydrogen project initiated by SGN aims to test the viability of a hydrogen gas grid. One of the issues of potential concern is the choice of odorant for hydrogen, as it is unlikely that the sulfur-based odorants commonly used in the existing gas grid are compatible with FCEVs. The aim of this work is to carry out preliminary screening of five candidate odorants for the hydrogen gas grid by assessing their short term impact on PEM fuel cell performance.
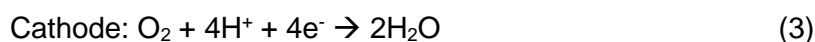
2   FUEL CELLS

A fuel cell is an electrochemical device that converts the chemical energy stored in a fuel directly to electrical energy with no combustion step, making it much more efficient than an internal combustion engine. When hydrogen is used as the fuel, it combines with oxygen from air to generate electricity with water as the by-product, according to the overall reaction:

$$2H_2 + O_2 \rightarrow 2H_2O \qquad\qquad (1)$$

The three main components of a fuel cell are the anode, the cathode and the electrolyte. In a typical PEM fuel cell, hydrogen is oxidised into protons at the anode. The protons migrate through the electrolyte to the cathode and combine with oxygen at the cathode to form water.

The electrons are forced to travel via an external path, completing the circuit and generating electrical power.

$$\text{Anode: } 2H_2 \rightarrow 4H^+ + 4e^- \tag{2}$$

$$\text{Cathode: } O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{3}$$

The PEM fuel cell is one of several varieties of fuel cell and is typically employed in the mid-range of power (up to ~200 kW). It employs a thin hydrated perfluorosulfonic acid-based membrane, which makes the overall size quite compact. The main catalyst component is platinum, which has a high affinity for the reactants, but not high enough for product species to block the active sites post-reaction. PEM fuel cells can operate at a relatively low temperature (< 100 °C) without any especially corrosive chemicals circulating in the system, which makes them highly favourable for automotive applications.

In general, there are three main sources of voltage loss in a PEM fuel cell: catalyst kinetics, ohmic losses and mass transport. The inherently sluggish kinetics of Reaction (3) are responsible for a significant loss of cell voltage, which is the dominant contribution at low current densities. Ohmic losses arise principally from proton transport in the membrane; the membrane resistivity is higher if the membrane is insufficiently hydrated. For this reason the inlet gases are often humidified, although if too much water is present, flooding of the pores in the catalyst layer can block access of reactant gas to the active sites. Ohmic losses generally dominate the losses at mid-range current densities. At high current densities, mass transport limitation occurs when there is insufficient supply of reactant to the active sites.

One of the major issues with PEM fuel cells is their relatively low tolerance to impurities, particularly on the anode (hydrogen) side. Sulfur-containing compounds such as mercaptans and sulfides adsorb strongly on platinum and can permanently block active sites, reducing the rate of Reaction (2). Hydrogen sulfide concentrations as low as 50 ppb have been observed to cause catalyst poisoning within a 200 h window.[2] In addition, large organic compounds such as diethylene glycol monomethyl ether, diethylene glycol monoethyl ether acetate and benzyl alcohol have been found to cause voltage loss by occupying active catalyst sites, even at low current density (0.2 A cm^{-2}).[5] Organic contaminants that interact strongly with the sulfonic acid group in the ionomer, such as aniline, can also degrade performance by substituting protons in the PEM, lowering the effective ionic conductivity.[6]

3   EXPERIMENTAL

3.1 TEST SET-UP

A single cell PEM fuel cell of active area 50 cm^2 was used to carry out preliminary screening of the five candidate odorants. The membrane electrode assembly (MEA) was supplied by FuelCell Store and was composed of a 25 μm thick Nafion 211 membrane, an anode catalyst layer with 20 wt.% Pt/C at a loading of 0.5 mg cm^{-2} and a cathode catalyst layer with 40 wt.% Pt/C at a loading of 0.5 mg cm^{-2}. A polytetrafluoroethylene(PTFE)-treated gas diffusion layer equipped with a microporous layer (SGL 29 BC) was used on both anode and cathode sides of the cell. Graphite flow-field plates with six parallel serpentine channels of 1 mm × 1 mm in cross-section were used on both anode and cathode, configured in partial counter-flow mode. The cell was compressed using a piston arrangement on the cathode side, with an applied pressure of 7 barg.

All tubing and fittings used in this work were coated with an inert Sulfinert (Thames Restek) coating to minimise depletion of odorant concentration due to adsorption on the stainless steel walls. However, due to time constraints associated with delivery of some coated components,

an exception was made for PTFE-lined valves and fittings and also for the pressure regulators.

All experiments were controlled by a fully calibrated Hydrogenics FCATS G50 test station. An external Sulfinert-coated mass flow controller (Bronkhorst) was employed to control the flow rate of the hydrogen/odorant gas mixture. The cathode was fed with zero grade air at 100% relative humidity (RH), while the anode feed was fitted with a Swagelok four-way valve to enable switching between dry hydrogen (99.9995% purity) generated from a hydrogen generator (Proton Onsite S40, USA) (0% RH) and the dry hydrogen/odorant gas mixture (0% RH). The cell was operated at 80 °C with both incoming gas lines heated to 85 °C to prevent water condensation. The cell was operated at ambient pressure and the gas stoichiometry was 2, for both anode and cathode. The process flow diagram for the experiment is shown in Figure 1. A three-way valve was employed on both the pure hydrogen and zero grade air supplies to enable switching to nitrogen purge when required. All gas lines were supplied with nitrogen during heating of the gas lines, humidifier and cell to their designated temperatures. The hydrogen/odorant gas line was purged with pure hydrogen for at least 24 hours prior to each experiment to minimise cross-contamination.
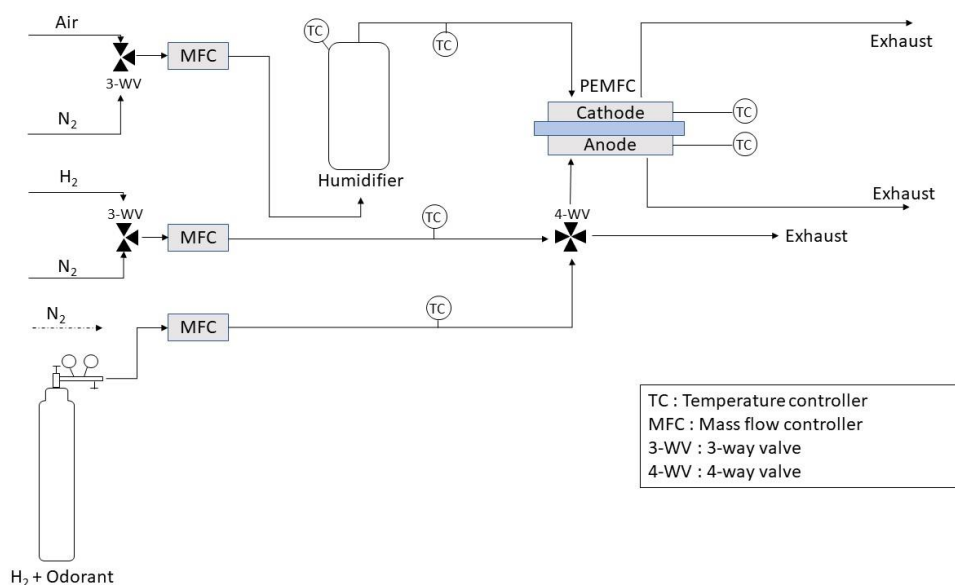

Figure 1. Process flow diagram for fuel cell screening test.

3.2 ODORANT GAS MIXTURES

Five different hydrogen/odorant gas mixtures were selected for testing, with odorant concentrations shown in Table 1. Prepared odorants were mixed with ultra-pure hydrogen (Air Products, BIP® PLUS grade) fulfilling the requirements of the ISO 14687 standard. Each hydrogen/odorant mixture was contained in a cylinder prepared exclusively for the project. Three of the odorants (NB, THT and NB dilute) contained sulfur compounds, while two (norbornene and acrylates) did not.

Table 1. Composition of the hydrogen/odorant gas mixtures tested (balance hydrogen).

Identifier	Components	Concentration
Norbornene	5-ethylidene-2-norbornene	17.06 ppm
Acrylates	Methyl acrylate	0.7 ppm
	Ethyl acrylate	1.12 ppm
	2-ethyl-3-methylpyrazine	0.05 ppm
NB dilute	2-methyl-2-propanethiol	0.5 ppm
	Dimethyl sulfide	0.2 ppm
	Hexane	1.3 ppm
THT	Tetrahydrothiophene	5 ppm
NB	2-methyl-2-propanethiol	1.5 ppm
	Dimethyl sulfide	0.4 ppm

3.3 TEST PROTOCOL

The protocol for quantifying the impact of each hydrogen/odorant gas mixture on PEM fuel cell performance was spread over 4 days of measurement as follows.

Day 1: Cell hardware cleaning, followed by cell assembly and activation of the MEA by operating the cell at 0.5 A cm^{-2} overnight.

Day 2: Beginning-of-life (BoL) characterisation of the cell, consisting of an ohmic loss (IR)-corrected polarisation curve with pure hydrogen at the anode.

Day 3: Odorant exposure test at 0.8 A cm^{-2}, during which the impact of the hydrogen/odorant gas mixture on both the cell voltage and the impedance response was monitored.

Day 4: End-of-life (EoL) characterisation of the cell, consisting of an IR-corrected polarisation curve under hydrogen/odorant gas mixture, after the cell had been fed with the hydrogen/odorant gas mixture at 0.8 A cm^{-2} for 30 minutes or until a lower limit of 0.1 V had been reached.

Between each measurement day, the cell was operated at 0.5 A cm^{-2} using pure hydrogen as the anode feed. A fresh MEA was used for each experiment.

The polarisation curve protocol comprised two stages: ramp-up and ramp-down. The ramp-up stage was performed by increasing the current density through defined incremental current density values, from 0 A cm^{-2} (open circuit) up to a current density corresponding to a cell voltage of 0.3 V. The dwell time at each current density was 2 minutes. Once a cell voltage of 0.3 V had been reached, the ramp-down stage was commenced. The current density was lowered incrementally through the defined current density values to open circuit with a dwell time of 5 minutes at each step. When recording the polarisation curve, the cell voltage was taken as the average value over the last 30 s at each current density step during the ramp-down stage. The polarisation curve was corrected for IR losses using impedance measurements recorded at each current density over a frequency range of 100 kHz to 1 kHz with an amplitude of 10% of the applied current. The cell resistance for IR correction was taken as the value of the real part of the impedance (Z_{real}) when the imaginary part of the impedance ($Z_{imaginary}$) is zero.

The odorant screening test protocol consisted of three stages: (i) baseline, (ii) contamination and (iii) recovery. In the baseline stage, the cell voltage was monitored for 1 h while supplying pure hydrogen to the anode at an applied current density of 0.8 A cm^{-2}. This relatively high

current density was chosen based on a report commissioned by the US Department of Energy to evaluate the effect of organic contaminants on PEM fuel cell performance, which was designed to replicate conditions in an operating FCEV[7]. For the contamination protocol, the anode feed was switched from pure hydrogen to the hydrogen/odorant gas mixture and the cell voltage was monitored for 4 h. In preparation for the contamination stage, the odorant gas mixture was flowed at 0.21 normal litres per minute (0 °C, 1 atm) for 30 minutes through a bypass line to achieve a steady-state temperature and to saturate any potential odorant adsorption on the tubing. Finally, during the recovery protocol, the anode feed was switched back to pure hydrogen for 2 h. Electrochemical impedance spectroscopy (EIS) measurements were carried out over the frequency range 100 kHz to 10 mHz at the end of each stage.

4   RESULTS

4.1 BoL CHARACTERISATION

IR-corrected polarisation curves obtained with pure hydrogen at the anode at BoL for all five MEAs are presented in Figure 2. Good repeatability is observed in the polarisation curves, with a cell voltage variation of < 10 mV between different MEAs, which provides confidence in the inter-comparability of the data from different tests.
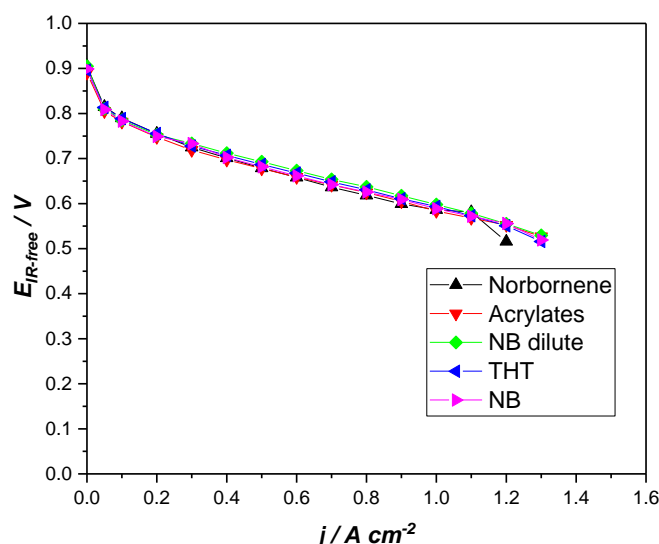
Figure 2: IR-corrected polarisation curves of the five MEAs at BoL (80 °C, 1 atm, stoichiometry anode and cathode: 2, anode: 0% RH, cathode: 100% RH).

4.2 CELL VOLTAGE MONITORING

The evolution of cell voltage as a function of time in the presence of the five different hydrogen/odorant gas mixtures at the anode is presented in Figure 3. The three stages of the contamination protocol are indicated: (i) 1 h baseline with pure hydrogen, (ii) 4 h exposure to hydrogen/odorant gas mixture, (iii) recovery with pure hydrogen. The magnitude of the drop in cell voltage during the 4 h exposure to the hydrogen/odorant gas mixtures is summarised in Table 2, along with the cell voltage recovery upon restoration of pure hydrogen for 2 h. The three sulfur-containing hydrogen/odorant gas mixtures (NB, THT and NB dilute) caused a significant and predominantly irreversible cell voltage decay during the 4 h exposure period,

demonstrating that they are incompatible with PEM fuel cell operation. In contrast, the rate of cell voltage decay for the non sulfur-containing odorant gas mixtures (norbornene and acrylates) was within the range observed in pure hydrogen in the 1 h baseline period (up to 3 mV h^{-1}), making it difficult to determine conclusively that there is no detrimental effect of their presence. The 1 h baseline period is not sufficient to establish a steady-state cell voltage decay rate, which would be expected to be significantly lower than this.[8] It can be concluded that while this short term screening test is suitable for ruling out odorants with a significant detrimental effect on PEM fuel cell performance, longer term testing is required to provide more conclusive qualification of more promising odorants.
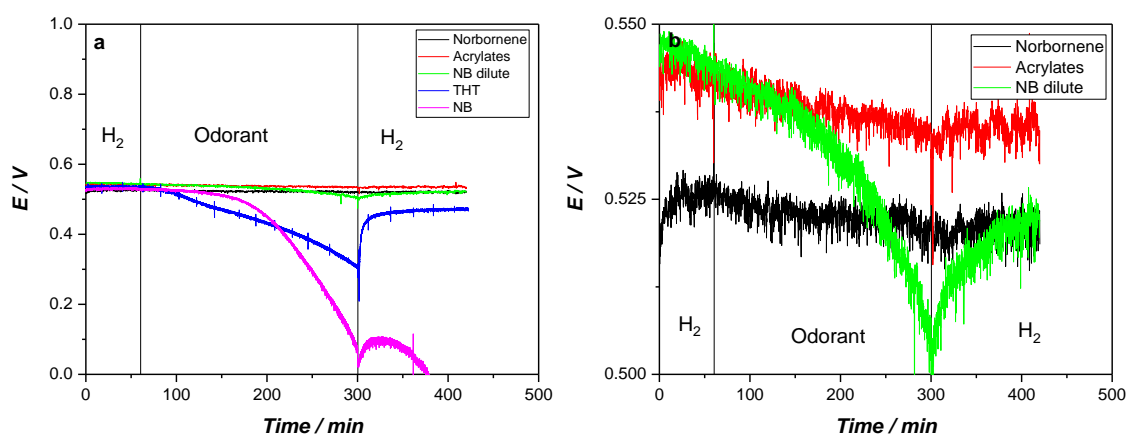
Figure 3: (a) Evolution of cell voltage with time during screening of the five hydrogen/odorant gas mixtures at 80 °C and 0.8 A cm^{-2} and (b) the same data for three of the hydrogen/odorant gas mixtures (norbornene, acrylates and NB dilute) on an expanded scale.

Table 2. Summary of cell voltage loss and recovery in odorant screening tests (to nearest mV).

Identifier	Cell voltage loss after 4 h (mV)	Cell voltage recovery after 2 h (mV)
Norbornene	5 ± 2	0
Acrylates	10 ± 2	0
NB dilute	40 ± 2	20 ± 2
THT	225 ± 2	175 ± 2
NB	460 ± 2	0

4.3 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

The results of EIS measurements conducted at the end of baseline, contamination and recovery stages are presented in Figure 4. At the end of the baseline stage, an impedance spectrum was observed with two characteristic arcs corresponding to the kinetics of the anode and cathode reaction (left arc, higher frequencies) and losses from mass transport of dissolved reactant gas (right arc, lower frequencies).[9] The impedance spectra after the contamination stage are consistent with the results of the cell voltage monitoring tests, with the largest

changes observed in the presence of NB and THT. For both of these odorants the arc associated with the kinetics of the anode reaction, which is not visible under normal operating conditions, dominates the impedance spectrum. For both norbornene and acrylates it was difficult to distinguish the contaminated spectrum from the baseline spectrum, which supports the view that longer term testing is required to provide a more discriminating test.
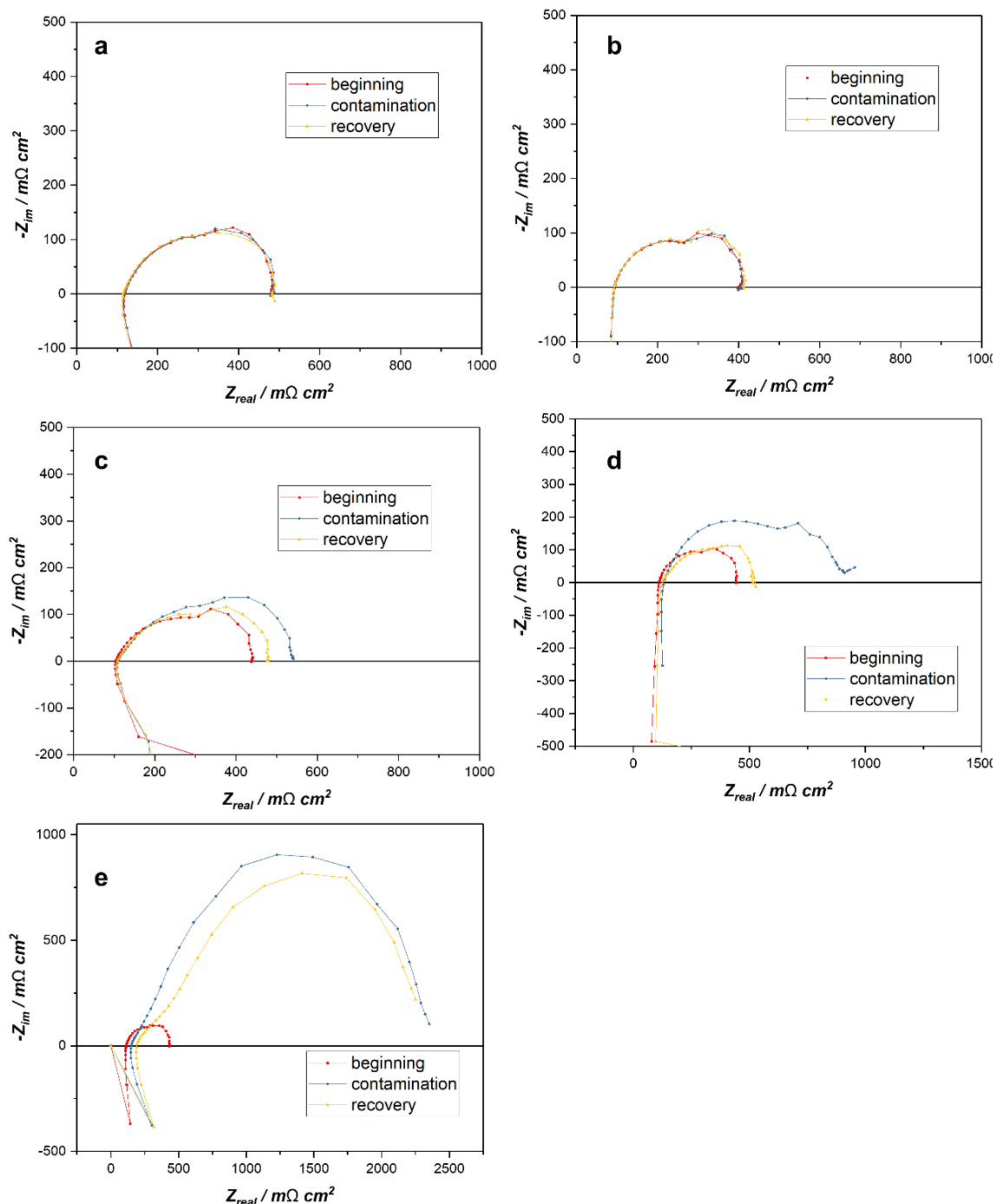

Figure 4: EIS spectra recorded at the end of the baseline, contamination and recovery stages of the odorant screening tests in the presence of (a) norbornene, (b) acrylates, (c) NB dilute, (d) THT and (e) NB.

4.4 POLARISATION CURVES

IR-corrected polarisation curves of the fuel cell before and after odorant exposure are shown in Figure 5. The trend in the results is consistent with the cell voltage monitoring tests and impedance measurements, with significant losses ascribed to the kinetics of the anode reaction in the presence of THT and NB.
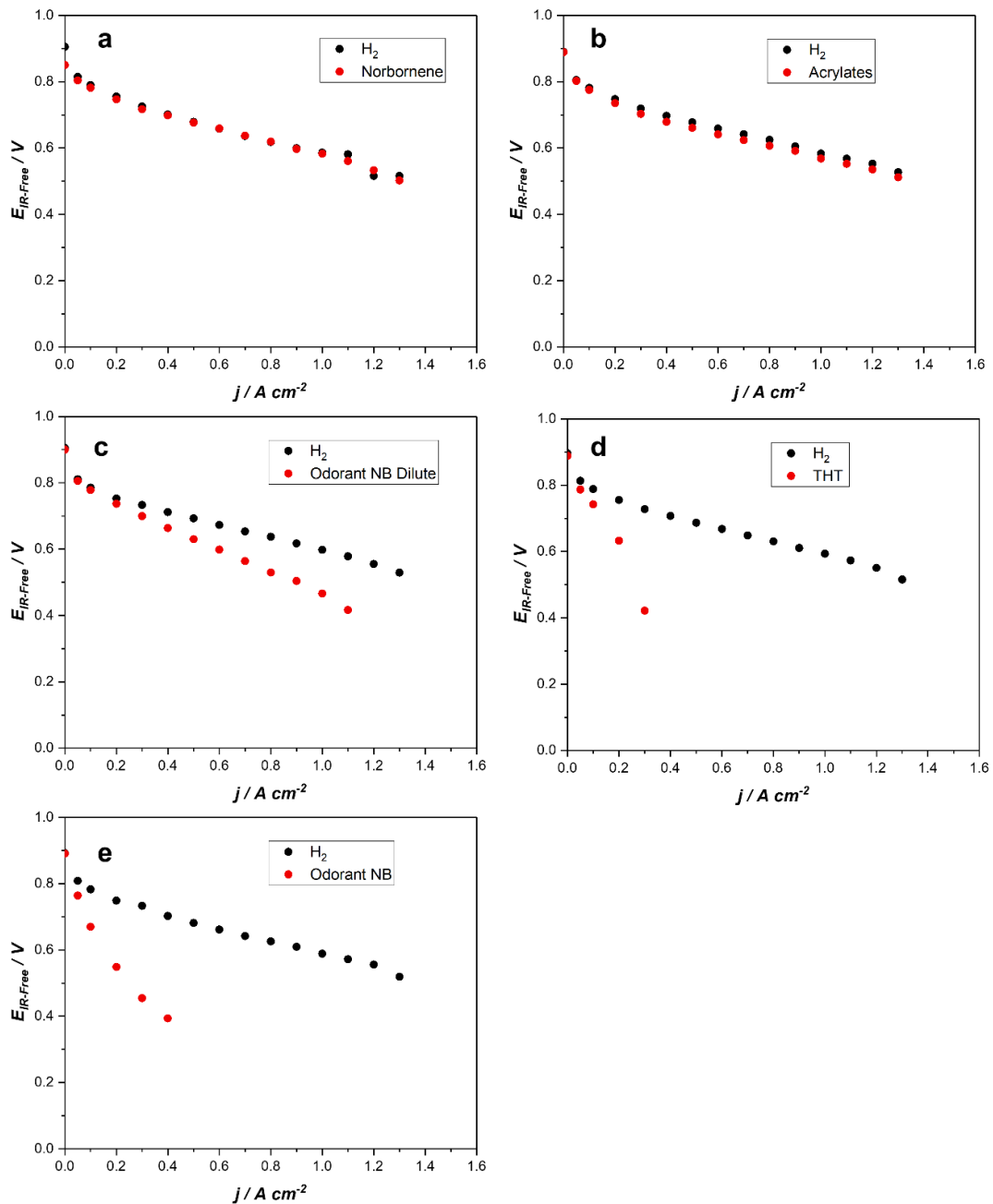

Figure 5: Comparison of IR-corrected polarisation curves at BoL (under pure hydrogen) and under hydrogen/odorant mixture (after 30 min continuous exposure) with (a) norbornene, (b) acrylates, (c) NB dilute, (d) THT and (e) NB.

5   CONCLUSIONS

Preliminary screening of five candidate odorants for the hydrogen gas grid was carried out using single cell fuel cell testing. The three sulfur-containing odorant gas mixtures (NB, THT and NB dilute) were found to be incompatible with PEM fuel cell operation. It was not possible to determine conclusively that there was no detrimental effect of the non sulfur-containing odorant gas mixtures (norbornene and acrylates) due to the relatively low cell voltage decay rate and the short term nature of the test. A significantly longer test duration for both the baseline tests in pure hydrogen and the odorant exposure tests is recommended to provide more conclusive qualification of these odorants.

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Techno-economic comparative assessment of hydrogen odorants

Final Report

Version V1.2

E4tech (UK) Ltd for the National Physical Laboratory

October 2019

E4tech

Strategy | Energy | Sustainability

Contents

1 Introduction

1.1 Background

Decarbonisation of heat will be a crucial element of the UK's drive towards its target of net zero carbon emissions by 2050. One possible solution to reducing carbon emissions from heat is to replace natural gas with zero or low carbon hydrogen in the existing gas grid, offering the prospect of a largely decarbonised heat solution.

Several projects are underway to examine the feasibility of moving to a 100% hydrogen gas grid in the UK and elsewhere. One such project, Hydrogen100 (H100) funded by Scottish Gas Networks (SGN), is investigating all aspects of such an undertaking including the safety case, the regulatory regime and the economic costs. Since hydrogen is a colourless and odourless gas, an important consideration when making the safety case will be the use of an odorant to allow leaks to be detected by smell as is currently the case with natural gas.

As part of the SGN funded Hydrogen 100: Hydrogen Odorants and Leak Detection project, NPL was asked to perform a review of relevant standards and regulations relating to odorants in order to provide suitability criteria for an odorant that could be used within the UK's 100% hydrogen grid. This yielded a recommendation of five potential candidate odorants, as chosen by SGN, to be evaluated by the following criteria.

- Olfactory characterisation;
- Fuel cell degradation;
- Pipeline corrosion (both metal and plastic piping);
- Boiler corrosion;
- Stability; and
- Health and environmental effects.

Alongside this technical analysis, an economic assessment has been carried out by E4tech Limited to evaluate the cost of using each of the proposed odorants in comparison with the cost of the current odorant used in the natural gas network.

This study was designed to identify any differences in the underlying capital and operating costs relating to the odorant delivery system itself and to provide an estimate of the cost of any degradation to pipelines and / or end-use appliances.

1.2 Aims and objectives

As indicated in Section 1.1, the primary aim of the economic study was to establish whether the use of the selected odorants with hydrogen in a 100% hydrogen grid would result in a change in the cost of operating the grid relative to the current natural gas grid. Only costs attributable to the use of the odorants with hydrogen were accounted for and compared with the cost of using the current odorant with natural gas.

An Excel Spreadsheet model was developed and used in order to establish the extent and range of cost impacts on an annual and energy throughput basis. The economic model drew on data from the technical study carried out by NPL and other data from third parties relating to aspects such as the cost of the odorant systems themselves.

It is important to note that while the study is intended to provide perspective on the potential cost impact of a UK-wide implementation of a 100% hydrogen grid, the model has been built to reflect the system being engineered for the H100 project. Caution should therefore be used when extrapolating these results since the relative cost per unit of energy delivered might change as the network size is increased. However, the model provides a first approximation of any changes in relative costs

1.3 Structure of report

In section 2 we describe the method applied and the data gathered; in section 3 we present the results of the analysis; and in section 4 we summarise our conclusions and offer recommendations.

2 Methods and data

2.1 Definition of scope and model boundaries

As discussed, part of the H100 project experimental work was conducted aimed at testing the effect of five different odorants on hydrogen pipelines, boilers and fuel cells. This was, in conception, compatible with a range of possible scenarios for large scale use of hydrogen fuel in the UK, including the following:

- Centralised or distributed production of hydrogen, transmission to the whole of the UK via the gas grid and use in buildings for heating in flame boilers;
- Centralised or distributed production of hydrogen, transmission to the whole of the UK via the gas grid and use in buildings for heating in flame boilers and for micro combined heat and power (mCHP) in fuel cells (FC); and
- Centralised or distributed production of hydrogen, transmission to the whole of the UK in the gas grid and use in buildings (boilers and/or CHP FC) and as a transport fuel in fuel cell vehicles.

For each of these scenarios, estimating the economic impact of using hydrogen odorants at a system level requires an understanding of the additional costs they engender, starting from their storage and injection in the hydrogen grid to their end use or removal prior to the hydrogen end use.

In particular, in the case of hydrogen used for heating/hot water in buildings where the hydrogen is directly fed to flame boilers, we expect that the odorant will probably *not* need to be removed from the hydrogen prior to its final use, and that the presence of an odorant will unlikely result in very rapid degradation of a gas boiler. However, in the case where the odorant is to be used in a PEM FC, significant degradation could be envisaged. To arrive at a manageable model, we have defined a central scenario and have flexed the parameters to observe the effect of doing this on the outputs.

It is critical to reiterate that the purpose of the study and the associated model is not to compare the costs of a hydrogen-based network with a natural gas network per se but *only* to model the cost differential relating to the use of an odorant with hydrogen as compared with using an odorant with natural gas.

Three principal potential sources of cost differential were identified as follows:

1. Changes to the capital or operating cost of the odorant system itself. For example, the number or size of injection units or the volume of odorant required might change altering the capital or operating costs respectively.
2. Changes to the rate of degradation of equipment carrying or using the hydrogen. For example, the lifetime of pipelines carrying hydrogen or the number of boiler failures requiring maintenance might change. This could alter the capital expenditure or operations and maintenance cost of the overall heating system.
3. The addition or removal of other equipment in the network not immediately related to the odorant system itself. For example, additional purification might be required to remove the odorant before the hydrogen is used in a fuel cell connected to the hydrogen grid increasing the overall capital and / or operating costs accordingly.

In developing the model, we first established whether the introduction of the odorant had any effect on the performance of the system and then sought to establish whether this change in performance is greater or smaller than the resultant change in the control system (i.e. the existing odorant with natural gas).

For example, it is well understood that the use of the natural gas odorant, NB, results in the formation of an acidic condensate within boilers when natural gas is combusted and these appliances have been designed with that in mind. Design life and expected failure modes reflect the presence of this corrosive liquid in the process and may result in a reduction in lifetime of, say 5%, compared with burning natural gas without the odorant. When making the comparison between the cost of using of the five selected odorants with hydrogen and the use of NB with natural gas we are only interested in this *change* in design life. It was shown through experimentation that an acidic condensate also formed when hydrogen was burned with sulphur containing odorants but from an economic modelling perspective we are only interested if this increases or decreases the lifetime by more or less than 5%.

In order to establish the economic cost of any change in lifetime reduction we need to establish the underlying cost of the system elements themselves even though the model is not comparing the costs of hydrogen and natural gas boilers per se. If, as may be expected, hydrogen boilers are costlier than their natural gas counterparts then more frequent replacements are relatively more costly than if the underlying capital costs are the same.

For each relevant system element, we have gathered the pertinent data from third party sources or from our proprietary knowledge. Where necessary we have made sensible engineering judgements and tested the sensitivity of outputs to changes to input parameters.

2.2 Model design and data

The model was originally envisaged as a comparison of the annual costs of investing in and operating the odorant system with the 100% hydrogen system with the equivalent natural gas system, taking into account both the cost of the odorant system itself and any impact on heating system elements.

The findings from the technical studies allowed us to make some immediate simplifications to the model compared to how it was originally conceived. The studies indicate *none* of the odorants when used in conjunction with hydrogen are likely to have appreciably more or less impact on the lifetime or operating and maintenance costs of boilers and pipelines than would the use of NB with natural gas.

By contrast, the sulphur containing odorants tested result in significant fuel cell degradation. We consider that the degree of degradation with these odorants is sufficiently great that they would have to be separated from the hydrogen before use in fuel cells. For the non sulphur containing odorants, the technical analyses were inconclusive. It was not possible to determine that there was *no* detrimental effect due to the relatively low cell voltage decay rate and the short term nature of the test. In consequence, we assume that these odorants would also have to be removed as well.

Consequently, pipeline, boiler and fuel cell costs could all be removed from the equation when structuring the model as the simplified model design pictured in the diagram in Figure 1 shows.
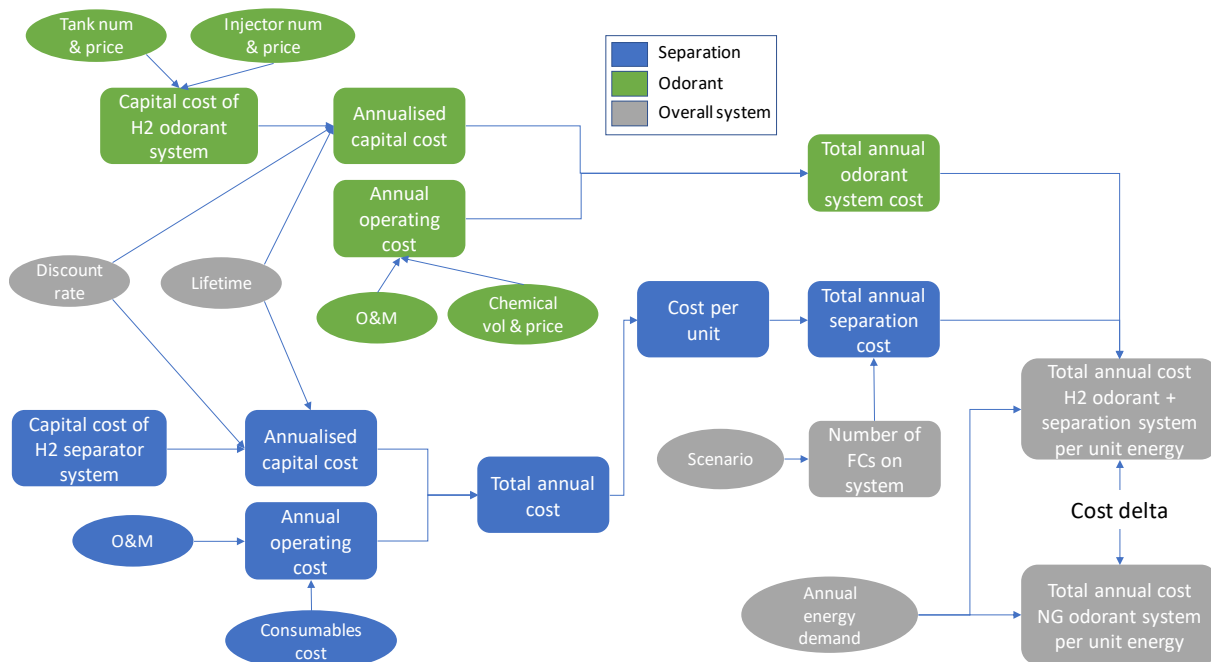
Figure 1 Diagrammatic representation of cost model

The model consists of four main Worksheets – Scenarios, Input, Annual Opex Calculation and Annual Capex Calculation – within an Excel Spreadsheet. A Cover sheet provides a brief description of the model and its purpose together with an indication of the purpose of each of the sheets. In addition, it gives the revision number and date. A sheet entitled Charts contains key graphical outputs from the model. There is a final sheet entitled MDAL which contains the Master Data & Assumptions List. The function of each Worksheet and the functioning of the model is described in Sections 2.2.1 to 2.2.5.

2.2.1 Scenarios

This sheet describes the scenarios considered in the model and displays the primary outputs from the model calculations for each of the four modelled scenarios. As will be discussed in Section 3.1, the scenarios are defined according to the relative proportions of the energy carried in the hydrogen network that is directed towards boilers and fuel cells. The parameters for the four defined scenarios are locked but an additional user defined scenario allows the user to explore the effect of altering the proportion of boilers (and indirectly the number of FCs) to a level other than the ones defined in scenarios 1 to 4. A screen capture of the Scenarios worksheet is shown Figure 2 below.
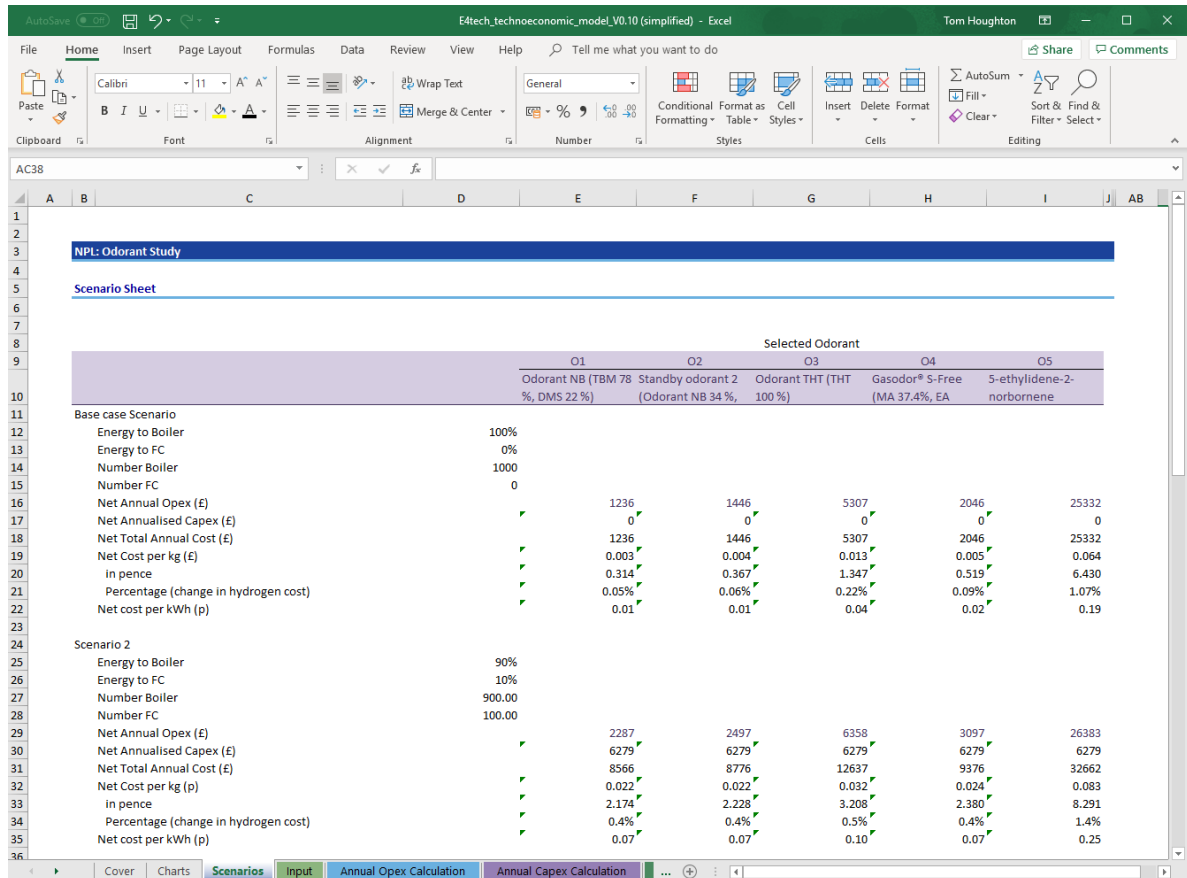
Figure 2 Screenshot of Scenarios Worksheet

The input parameter settings for each scenario appear column D while the output values for each odorant appear across columns E – I. Costs are output in terms of annual operating costs, annualised capital expenditure, total annual costs (being the sum of these two elements) and the total cost per kilogramme of hydrogen transported.

2.2.2   Input

The input sheet is the main repository of underlying technical and economic data relating to the odorant system and the wider energy system under consideration as well as other key parameters relating to the calculations.

The upper part of the sheet is shown in the screen capture below (Figure 3) and relates to the odorant system itself. The sheet is structured with the odorants under consideration arranged by column and the parameter labels by row. The 5 odorants tested with hydrogen occupy columns E – I, while column K is reserved for the reference natural gas odorant (NB). Rows are then organised into sections relating to the various parts of the system as described in the following sections.
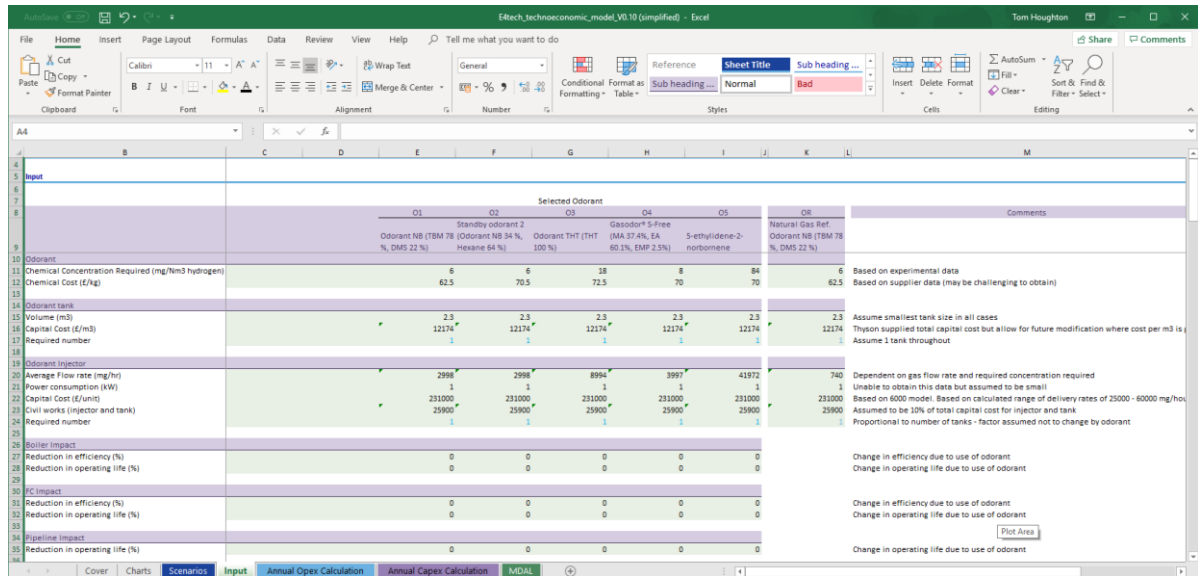
Figure 3 Screenshot of Input Worksheet (Upper)

Odorant

This provides the required concentration of each odorant in hydrogen (or natural gas) in mg/Nm3 together with the indicative cost per kg of these odorants. Note that we were unable to obtain comparable costs for odorants 4 and 5 but have estimated these based on discussions with relevant experts (see Table 1).

Table 1 Odorant parameters

	Odorant NB (TBM 78 %, DMS 22 %)	Standby odorant 2 (Odorant NB 34 %, Hexane 64 %)	Odorant THT (THT 100 %)	Gasodor® S-Free (MA 37.4%, EA 60.1%, EMP 2.5%)	5-ethylidene-2-norbornene	Natural Gas Ref. Odorant NB (TBM 78 %, DMS 22 %)
Concentration (mg/Nm3 H2)	6	6	18	8	84	6
Cost (£/kg)	62.5	70.5	70.5	70	70	62.5

Odorant tank

The odorant system has been split into two elements, the tank and the injector, to allow potential differences in the parameters relating to these elements to be modelled separately for each of the odorants (see Table2).

The volume of the tank can be specified for each odorant as can the number of tanks and the cost per unit of tank volume (£/m3), allowing for the possibility that the odorant tank may need to be designed with different characteristics according to the amount or nature of the odorant to be delivered. In practice, our working assumption is that there would be 1 tank per injection unit in all cases and that the size and unit cost of the tanks would be the same for all odorants. This implies

that for odorants required in higher concentrations, more frequent tank filling would be necessitated although this is not explicitly modelled.

Table 2 Odorant tank parameters

Volume (m3)	2.3
Capital Cost (£/m3)	12,174
Required number	1

Odorant injector

The number and capital cost of the injector system can be specified for each odorant as can the energy consumed by the injector as shown in Table 3. The model assumes that the energy consumed is directly proportional to the flow rate of the liquid being injected, irrespective of the actual composition of the odorant liquid. The required odorant flow rate is the product of the concentration required and the *average* hydrogen flow rate in the system (see discussion below). The capital cost of the injector assembly or the number of injector assemblies can be adjusted for each odorant to allow for different unit sizes or flow rates and so on.

In practice, our working assumption is that the capital costs and number of units are equal across all the odorants. We were unable to obtain data on the energy consumed so we assumed a power consumption of 1kW and an annual capacity factor of 0.2.

Table 3 Odorant injection unit parameters

	Odorant NB (TBM 78 %, DMS 22 %)	Standby odorant 2 (Odorant NB 34 %, Hexane 64 %)	Odorant THT (THT 100 %)	Gasodor® S-Free (MA 37.4% EA 60.1% EMP 2.5%)	5-ethylidene-2-norbornene	Natural Gas Ref. Odorant NB (TBM 78 %, DMS 22 %)
Average Flow rate (mg/hr)	2998	2998	8994	3997	41972	740
Power Consumption (kW)	1	1	1	1	1	1
Capital Cost (£/unit)	231000	231000	231000	231000	231000	231000
Civil works (injector and tank)	25900	25900	25900	25900	25900	25900
Required number	1	1	1	1	1	1

Boiler Impact, FC Impact and Pipeline Impact

As discussed, the model allows the cost of system degradation resulting from the use of the selected odorants with hydrogen to be estimated. This has been incorporated in the model by means of two parameters: a percentage reduction in lifetime and, if relevant, a reduction in operating efficiency (boiler and FC only).

In practice, zero values have been attributed to all these parameters since no impact on either boilers or pipelines has been observed and our working assumption is that odorants would be removed before reaching the fuel cell.

The lower part of the Input sheet with the heading Assumptions contains input data that are common across all the odorants (see screen capture in Figure 4). These are also organised by category and are described in the following sections.
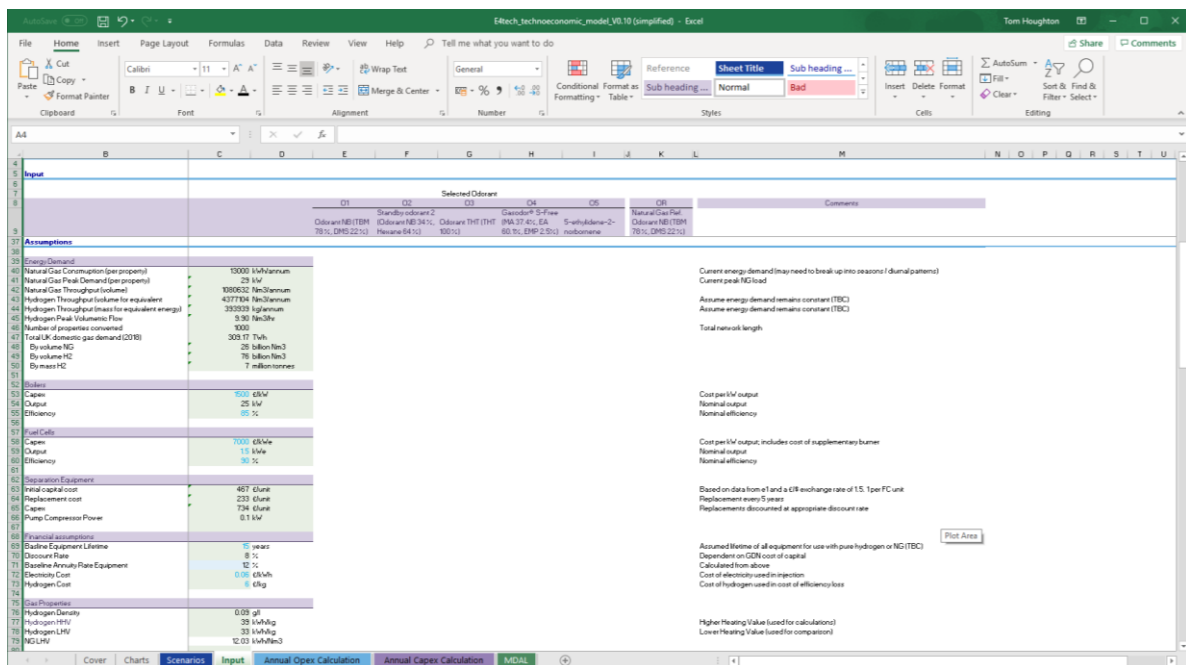

Figure 4 Screenshot of Input Worksheet (Lower)

Energy Demand

The energy demand used in the model is predicated on the small-scale demonstration proposed as part of the H100 project. This comprises 300 homes initially rising to 1000 homes in the second phase and the higher number has been used in the underlying model. Details are shown in Table 4.

The total annual hydrogen demand (by mass) is then calculated based on the current average gas demand per property *in energy terms* in the relevant region and the lower heating value of hydrogen in kWh per kg. The total annual volume of hydrogen required is then calculated based on the annual mass of hydrogen and the density at standard temperature and pressure.

This annual volume demand is in turn used to calculate an average odorant injection rate assuming a constant flow rate throughout the year. Clearly this is only an approximation as we know that the gas flow rate varies significant over the course of the year and indeed the course of any given day.

Consequently, we have included a row for peak energy demand per property which is used to calculate a peak flow rate of hydrogen for the entire energy system. It is set equal to the peak boiler output divided by the boiler efficiency (see below), although this could be modified if data on peak hydrogen demand were available. At present this peak demand figure is not used elsewhere in the model but could be used in a more sophisticated representation of injector sizing and cost if required. However, we consider that the use of an average annual flow rate is an acceptable approximation since the cost of the injector does not vary significantly enough as a function of flow rate.

Table 4 Gas system parameters

Natural Gas Consumption (per property)	13000	kWh/annum
Natural Gas Peak Demand (per property)	29	kW
Natural Gas Throughput (volume)	1080632	Nm3/annum
Hydrogen Throughput (volume for equivalent energy)	4377104	Nm3/annum
Hydrogen Throughput (mass for equivalent energy)	393939	kg/annum
Hydrogen Peak Volumetric Flow	9.90	Nm3/hr
Number of properties converted	1000	

Boilers

The hydrogen boiler peak output and efficiency can be set in this section and these values are used to calculate the peak hydrogen demand as described above as shown in Table 5. They can also be used to calculate the cost attributable to changes in efficiency from degradation if any were noted. The peak output and efficiency values are based on those for an equivalent natural gas boiler. The boiler capital cost is only relevant to the overall capital cost calculation if boiler degradation is factored in so although this is included in the input sheet it is not used in the simplified model.

Table 5 Boiler parameters

Capex (£/kW)	1500
Output (kW)	25
Efficiency	85

Fuel cells

As with boilers, the peak output and efficiency can be set along with the capital cost as shown in Table 6. These are used, as with hydrogen boilers, to calculate the cost of degradation, if applicable. As previously indicated, we assume that the mCHP units or transport fuel cells are of PEM chemistry which is very sensitive to impurities (they typically require a hydrogen purity of at least 99.999%). Current mCHP units are typically of SOFC chemistry which are less sensitive to the presence of fuel impurities but these are not adapted for the use of hydrogen fuel.

Table 6 Fuel cell unit parameters

Capex (£/kWe)	7000
Output (kWe)	1.5
Efficiency	90

Separation equipment

As discussed previously, our working assumption is that if PEM fuel cells are directly connected to the gas grid then the odorants will need to be removed before the hydrogen passes into the fuel cell. The safety case would no doubt require that removal equipment is co-located with the FC in order to ensure that leaks can be detected as the gas passes through the property on its way to where the FC is positioned. Note in the case that the hydrogen pipeline network is used to supply transport fuel cells then purification would likely take place at the level of the refuelling station rather than at the individual fuel cell. The separation unit would need to be scaled accordingly and we assume that the cost per unit of hydrogen throughput would be roughly the same irrespective of the type of fuel cells connected to the network

It is expected that separation would be achieved through the use of membranes, pressure swing absorption or some kind of physical absorption method. The cost of the system would be made up of the annualised capital cost and the annual operating costs which would incorporate any running costs (e.g. electricity consumption) or maintenance costs, e.g. the replacement of membranes. A per unit capital cost and operating cost can be set for the separation unit with the operating cost being a function of the throughput of hydrogen. We were unable to obtain data on the required compressor energy consumption so we have estimated the compressor power consumption to be 0.1kW and a capacity factor of 0.2 (Table 7).

Table 7 Separator equipment parameters

Initial capital cost (£/unit)	467
Replacement cost (£/unit)	233
Capex (£/unit)	734
Pump Compressor Power consumption (kW)	0.1

Financial Assumptions

We have made the simplifying assumption that all equipment connected to the hydrogen grid, including boilers, fuel cells, separation equipment and the odorant system itself has the same lifetime, which we have nominally set at 15 years (Table 8). Again, the assumed discount rate, used in conjunction with the lifetime to arrive at the annuity rate, is common to the whole system and set at 10%.

The electricity cost used, for example, in the calculation of injector operating costs can be set as can the price of hydrogen. This latter is used to calculate the cost of any reduced boiler or FC efficiency which would lead to increased hydrogen consumption although, as noted, this is not incorporated in the model.

Table 8 Financial assumptions

Basline Equipment Lifetime (years)	15
Discount Rate	8%
Baseline Annuity Rate Equipment	12%
Electricity Cost (£/kWh)	0.15
Hydrogen Cost (£/kg)	6

Gas Properties

The basic properties of hydrogen (higher heating value, lower heating value and density) and natural gas (lower heating value) are included for use in various calculations. To be conservative, we use LHV throughout (see Table 9)

Table 9 Gas properties

Hydrogen Density (kg/m3)	0.09
Hydrogen HHV (kWh/kg)	39.4
Hydrogen LHV (kWh/kg)	33.3
NG LHV (kwH/Nm3)	12.03

2.2.3   Annual Opex Calculation

This sheet is one of 2 primary calculation sheets which together feed into the Scenarios output sheet to give the model outputs. It allows the total annual operating expenditure for the odorant system for each of the odorants to be calculated and compared with the cost of the equivalent natural gas system. A screenshot is shown in Figure 5.

Figure 5 Screenshot of Annual Opex Calculation Worksheet

There are three components of cost:

- Annual odorant consumption given by the product of the average hourly odorant flow (calculated in the Input sheet) and the cost of each odorant multiplied by the number of hours in the year. It is assumed that operation would be required 100% of the time. Note that in order to ensure continuous operation redundancy would need to be built into the system. We have not included an additional cost for this since the unit we have selected is oversized for the 1000 home system.
- Annual electricity cost given by the energy consumption of the injector system, the annual quantity of odorant injected (both from the input sheet) and the cost of electricity (no data was obtained on this but we made some sensible engineering assumptions).
- Other O&M costs calculated as 10% of the capital cost of the odorant system.

A base operating cost per kg of hydrogen is calculated based on the annual operating cost and the annual consumption of hydrogen. These costs are independent of the scenarios for the configuration of end-use devices.

In addition to the cost of running the odorant system a cost for running the odorant removal system is calculated for each odorant on a per FC unit basis. These costs are only incorporated into the total opex in the output sheet in scenarios where FC devices are present and have been assumed to be negligible.

2.2.4 Annual Capex Calculation

The Annual Capex Calculation sheet (see Figure 6) is organised in a similar way to the opex sheet. The annual capital cost of the tank and injector are calculated separately, summed and annualised using the base annuity rate.

The annualised capex for a single odorant removal unit is calculated based on the capex on the input sheet and the base annuity rate. These costs are only incorporated into the total capital cost in the output sheet in scenarios where FC devices are present.

Figure 6 Screenshot of Annual Capex Calculation Worksheet

2.2.5 MDAL

As mentioned above, the MDAL sheet contains a complete description of each of the named variables in the model including:

- Variable Name as it appears in the variable name box in the Excel
- A description of the variable
- The base value – this allows a user which has made changes to the values to return them to the base value – if applicable
- A description of the source used for the base value

A screenshot of the template is shown in Figure 7.
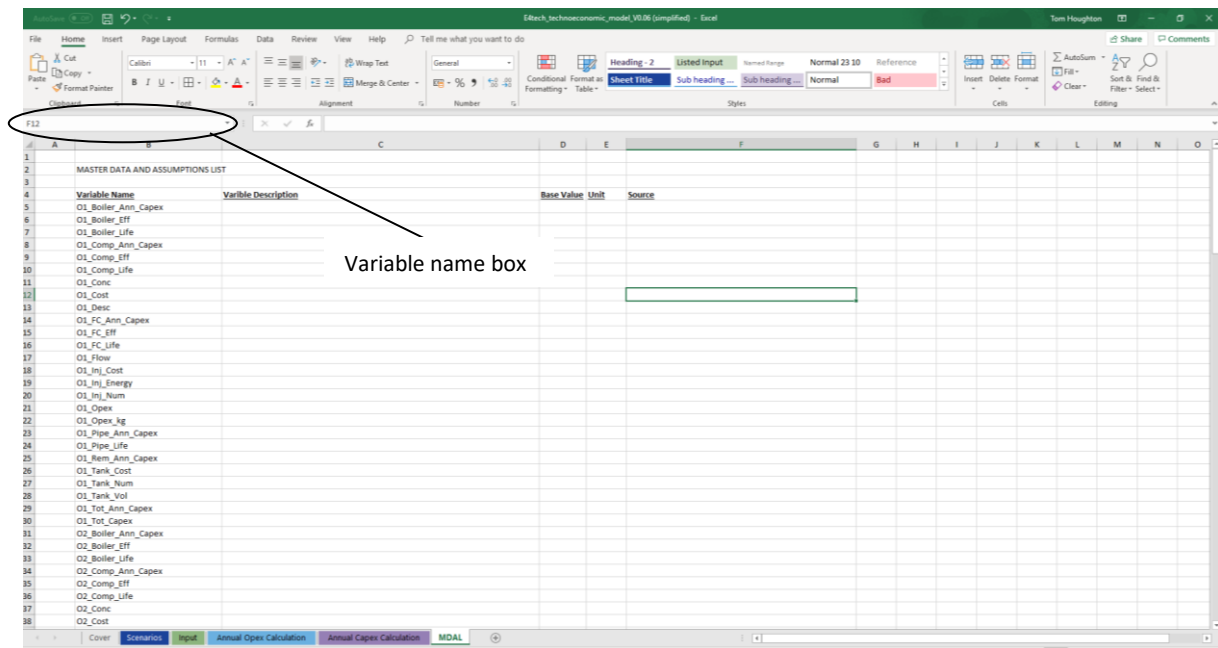
Figure 7 Screenshot of MDAL Worksheet

The complete list of the variables with a description, the value ascribed, if any, and the source of the value ascribed also appears in Appendix A.

Certain data proved very difficult to obtain, especially data concerning costs. Several factors underly and explain the paucity of data in certain areas:

- Commercially sensitive
- Experts unresponsive
- Hydrogen odorant system new
- H100 system yet to be designed

The data are necessarily speculative and subject to significant uncertainty. For this reason, we have flexed certain parameters around a base estimated value in order to observe the impact on the results.

3 Results and analysis

3.1 Scenario selection

We have selected a subset of scenarios for which to estimate the additional cost of odorising hydrogen relative to natural gas. These were discussed and agreed with NPL and reflect the uses of hydrogen that are deemed most beneficial and practically feasible in the UK. However, the model also allows users to define their own scenarios within certain boundaries.

The base case scenario for this study relies on the central assumption from the recent Committee on Climate Change CCC report into the contribution that hydrogen can make to the overall energy system. This analysis envisages that grid transported hydrogen is directed *only* towards heating. Further, according to the CCC the main use of pipeline hydrogen would be as a replacement to natural gas in buildings, where the hydrogen would be used in *flame boilers* that are part of hybrid heat pump/boiler systems. In such hybrid systems, the flame boiler is used to provide peak demand for heating/hot water that the electric heat pumps are not sized to meet. The scenario therefore entails the distribution of hydrogen to all buildings that are currently connected to the natural gas grid.

While not considered likely within the CCC analysis, an alternative heating solution involves the use of fuel cells connected directly to the network in a micro combined heat and power (mCHP) arrangement. In this instance, the fuel cell unit contributes both to the production of power for the home, exporting power to the grid if production exceeds demand, and providing base load heat (space and water) in a manner analogous to an electric heat pump. As with the hybrid heat pump/boiler system described above, the mCHP unit would also likely be combined with a boiler to provide peak heat load without oversizing the mCHP.

Several fuel cell chemistries exist for stationary fuel cells but for small applications where the fuel is hydrogen, the polymer electrolyte membrane (PEM) chemistry is arguably the most common. While PEM fuel cells have a number of advantages over other chemistries they require an extremely pure hydrogen stream which has implications for the use of odorants as will be discussed. In addition, hydrogen carried in the grid could be used to fuel road vehicles which also employ PEM FCs.

To reflect these use cases within the economic model, it is assumed that all hydrogen transported in the defined pipeline network is used either in boilers or PEM fuel cells. The scenarios are defined according to the relative proportion of energy carried is used in fuel cells or boilers connected to the network. The central case scenario assumes zero penetration of fuel cells on the network, as per the CCC report. Three additional scenarios have been defined within the Worksheet with fuel cell penetrations of 20%, 50% and 100%, to provide an assessment of the costs in the event that PEM fuel cells are connected directly to the network as part of a mCHP or transport refuelling arrangement. The scenarios are set out in more detail in Table 10.

Table 10 Scenario definition

Scenario	Boiler / FC penetrations	Logic
Base case	100% boiler, 0% FC	Corresponds with CCC scenario in which hydrogen in the gas network is only directed towards heat and only used in flame boilers
Scenario 2	80% boiler, 20% FC	Represents a case where hydrogen in the gas network is only directed to heating systems but where a proportion of hydrogen use is in mCHP fuel cell units
Scenario 3	50% boiler, 50% FC	Represents a case where hydrogen is being used primarily for heating and where there is a mix of boilers and FC mCHP units but a proportion is potentially also directed towards transport fuel
Scenario 4	100% FC	An extreme case where significant progress has been made in reducing FC costs meaning FC mCHP is the preferred solution for heating and where a proportion of hydrogen in the network is also directed to transport fuel

3.2 Initial comments on results

As discussed briefly in section 2.2, the initial findings from the technical degradation evaluation has led us to the following conclusions:

- No significant pipeline degradation is expected from the use of any of the odorants with hydrogen;
- Some degradation of boilers could be expected from the use of sulphur containing odorants with hydrogen but this would be no worse than would be expected from the use of the current odorant with natural gas;
- No boiler degradation would be expected from the use of the non sulphur containing odorants with hydrogen and performance could be better than the current odorant with natural gas, although this is unproven; and
- Significant degradation of PEM fuel cells was observed from the use of sulphur containing odorants with hydrogen while tests were unable to confirm that non sulphur containing odorants would not be detrimental to fuel cells.

These findings led us to suggest the following simplifying assumptions to the modelling:

- We consider it prudent to assume that no change to the lifetime of either boiler or pipeline results from the use of any of the odorants with hydrogen relative to the natural gas system (since the relationship between boiler degradation and failure modes has not been fully investigated); and

- Since the degradation of fuel cells is so severe in the case of sulphur-containing odorants we assume that these would have to be removed from the hydrogen before it is passed into a fuel cell. Furthermore, given that the results for the non sulphur-containing odorants were inconclusive we have assumed these would also have to be removed in our base assumptions.

We make qualitative comments about how changes in these assumptions would affect the results in the following results discussion where appropriate.

3.3 Base case scenario results and discussion

In the base case scenario no additional capital cost is incurred compared with the reference natural gas case and any differences observed reflect the change in operating costs due to, a) the cost of the odorant itself and / or b) the quantity of odorant required. The results for each odorant are shown in Figure 8.
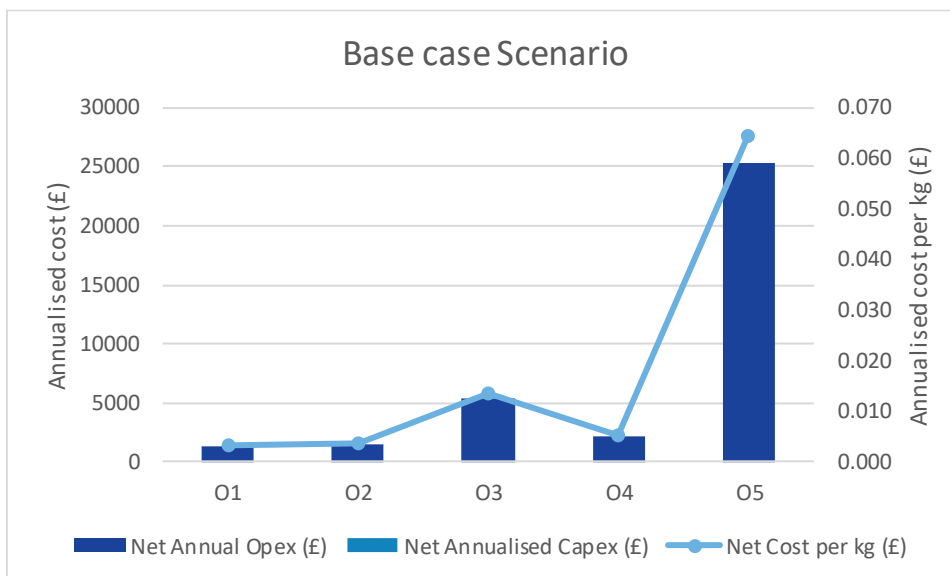

Figure 8 Annualised and per kg odorant costs in base case

The additional costs are modest reaching a maximum of 7 pence per kg of hydrogen, or 1.1% of the assumed cost of delivered hydrogen (£6 per kg) for the costliest odorant. For the other four odorants the additional cost ranges between 0.05% and 0.22% of the underlying hydrogen cost, with outputs for odorants 1, 2 and 4 being in a very tight range.

3.3.1 Whole system considerations

We have argued that when considering a network supplying 1000 homes, the sizing of the odorant unit would be the same for the hydrogen system and the natural gas system. This is because the amount of odorant to be deployed in either case lies within the capabilities of the smallest unit for which we have costs. In practice, a volume of hydrogen roughly 4 times the volume of natural gas is required to deliver the same amount of energy. The total number of odorant units required and the associated capital cost for a country-wide hydrogen system could be as much as 4x that for the natural gas system.

Based on the data gathered, we have calculated the lowest reasonable annualised cost of an odorant system per Nm3 of natural gas to be approximately 0.001p / Nm3. This is based on a total capex £300,000 for an odorant system able to deliver enough odorant for 10mNm3 per day[1] of gas throughput. If the throughput of hydrogen is roughly 4x the throughput of natural gas then this cost could rise to 0.004p / Nm3 or 0.044p / kg H2, giving an additional cost per kg of hydrogen of 0.043p or 0.01% of the underlying cost of hydrogen if considered across the whole system.

In practice the capital cost per volume of natural gas and hydrogen delivered will be higher than stated because the system will not be operated at its rated output all year (in essence it must be over-sized to be able to cope with peak demand). We partly account for this by assuming the throughput is lower than the rated output[2] but if we assumed that annual throughput was one tenth of the maximum potential throughput, the whole system cost per Nm3 of hydrogen would rise to 0.1% of the assumed hydrogen price. This would mean that the total increase in cost could be between 0.2 and 1.2% of the hydrogen cost when compared to natural gas, depending on the odorant used.

The hydrogen supply required to satisfy the entire annual domestic heating demand in the UK is roughly 7 million tonnes. Consequently, the cost increase if using odorant NB would represent an increase in total system cost of ~£84 million annually across the entire domestic demand for hydrogen.

3.4 Scenario results and discussion

In each of the subsequent scenarios there is a net increase in capital expenditure to reflect the need for separation equipment to remove impurities before the hydrogen is passed into the fuel cell. The net operating costs also increase slightly owing to the operating costs relating to the purification equipment. This is illustrated in Figure 9.

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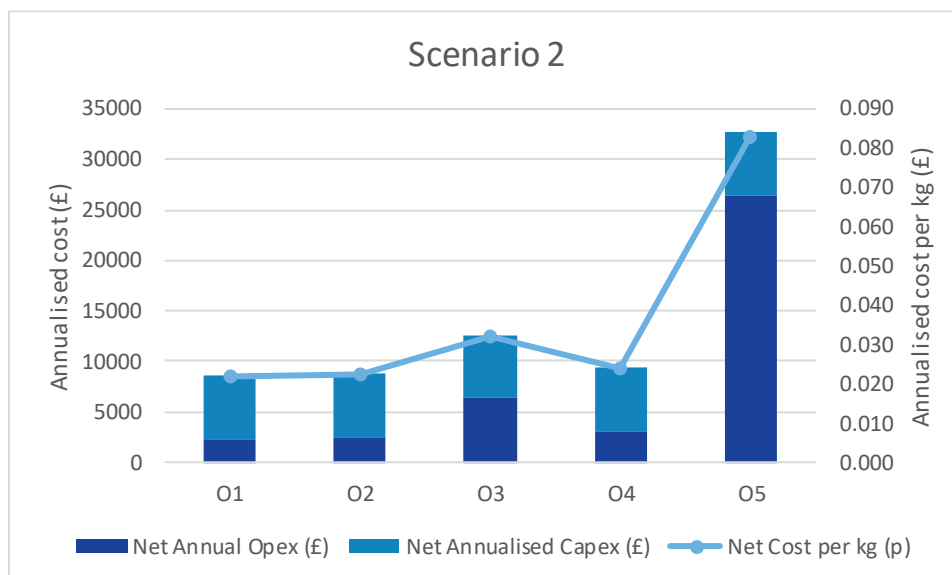
[1] Figures are based on the cost of the '8000 series' unit and the largest tank size quoted.
[2] We assume that the throughput is 10mNM3 per day although the max throughput that the system can handle is 13 m Nm3 per day.

Figure 9 Annualised and per kg odorant costs in base case

Annualised capital cost now has a significant impact and the net cost now varies between 2.2 and 8.3 pence per kg of hydrogen delivered or 0.4% and 1.4% of the underlying cost of hydrogen.

Using the same argument regarding whole system costs as was made for the base case with regards to the capital cost of the injection equipment for the entire network, we estimate the total net cost to be between 1 and 2% of the hydrogen cost per kg.

The net annualised capital expenditure increases as a function of the number of fuel cells connected to the system as does the operating costs relating to the purifiers. This is illustrated in Figure 10 where the total cost and cost per kg are shown for the base case scenario and scenarios 2 − 4 for odorant 1.
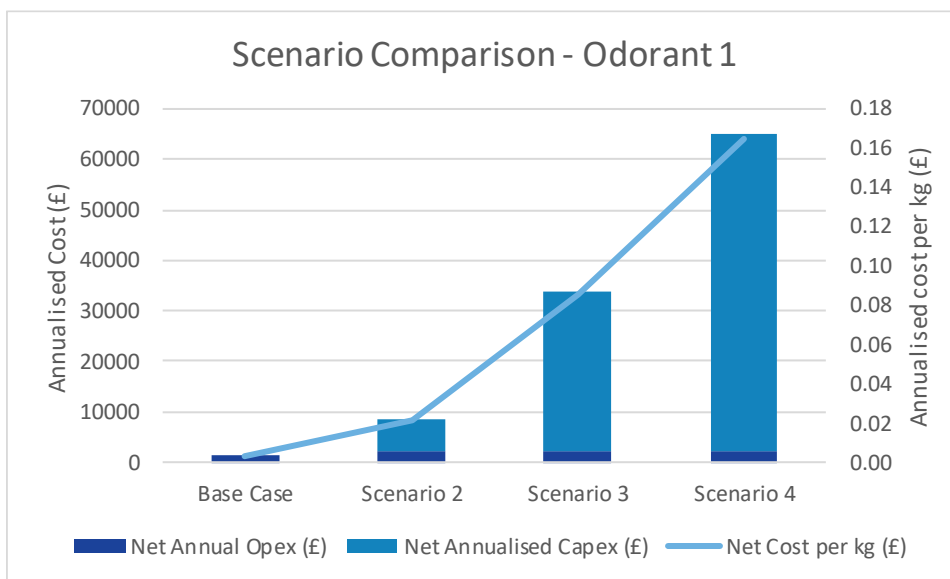

Figure 10 Annualised and per kg costs of odorant 1 in cases 1 − 4

The annualised cost per kg can now be quite significant and in scenario 4, where only fuel cells are connected to the gas grid, the cost per kg of hydrogen rises from 1p per kg of hydrogen delivered in the base case to as much as 16p. This represents 2.8% of the cost of underlying hydrogen and for the entire domestic heat demand would represent a total additional system cost of £1.1 billion annually.

3.5 Sensitivity analysis and discussion

As discussed, considerable uncertainty attaches to the input parameters and we have carried out sensitivity analysis to test the effect on the results of changes to certain of these parameters. We have considered them under the base case scenario and under scenario 2 which represents a case where a modest penetration of fuel cells is achieved.

We evaluated the sensitivity to the odorant cost, the capital cost of the separator and the discount rate; the results are shown in Figures 11 to 14.
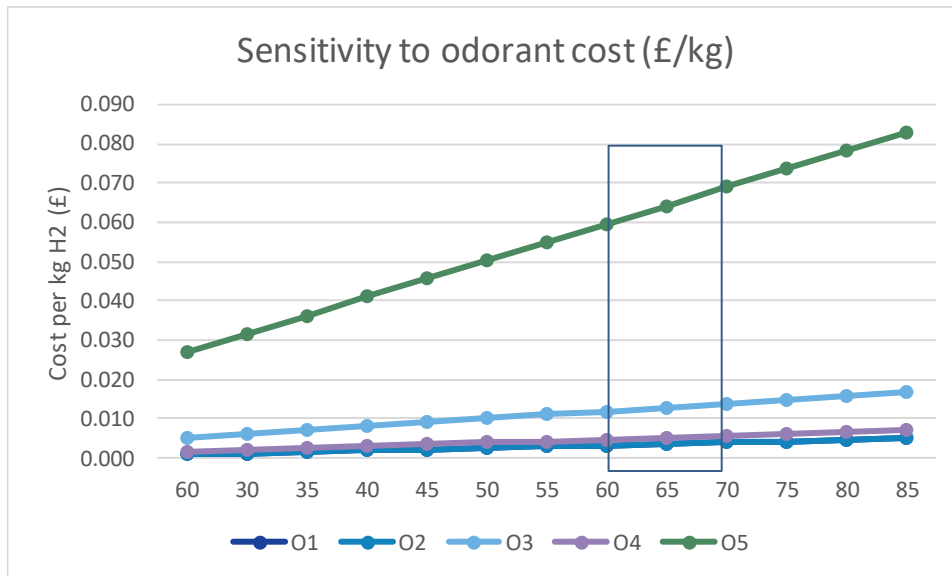
Figure 11 Sensitivity to odorant costs in base case scenario

In light of the fact that there is no net capex component to the system cost in scenario 1 the discount rate has no impact. Similarly, the lack of need for separation equipment makes the results insensitive to the separator capex.

The outputs are, however, sensitive to the odorant cost which we varied between approximately half and one and a half times the nominal cost (30 - 90 £/kg) of each odorant. This leads to between a ±67% change in the total net cost (odorants 1 and 2) and ±51%% for odorant 5 (see Figure 11).

In scenario 2, the total costs are sensitive to discount rate, separator cost and odorant costs. Once again, varying the odorant cost between 30 and 90 £/kg leads in odorant cost leads to between a ±35% change (odorant 5) and ±7% (odorants 1 and 2) change in total cost (Figure 12). The difference relative to the base case scenario is explained by the fact that the additional capital costs in scenario 2 dominate for odorants 1 and 2 which have lower odorant costs in absolute terms.
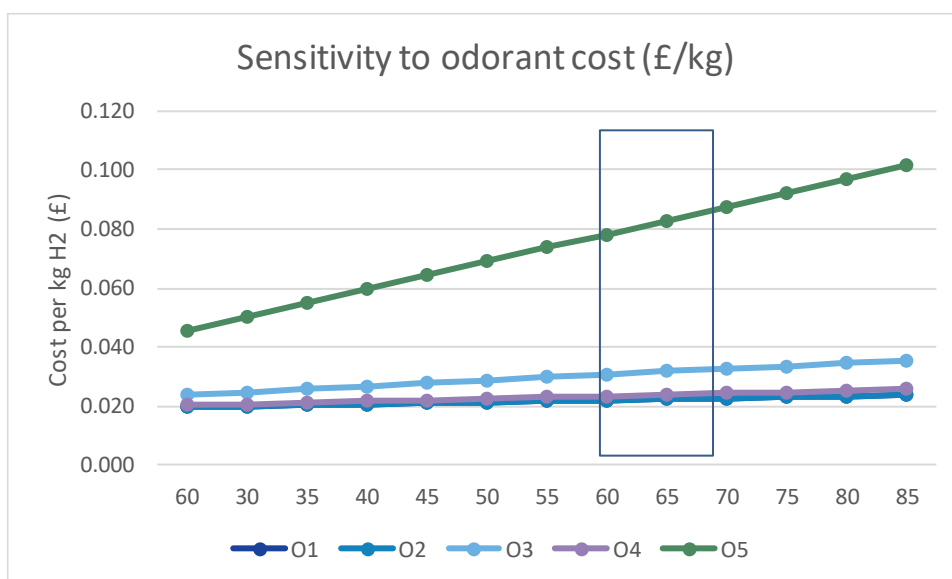
Figure 12 Sensitivity to odorant costs in scenario 2

We varied the separator cost per unit between roughly one quarter and 2 times the projected future cost per unit ($100 – 800). This generates a change in total costs for odorants 1 and 2 or +57%/-62% and +20%/-22% for odorant 5. The relatively higher sensitivity of odorants 1 and 2 is explained, once again, by the relatively higher proportion of capex in the total cost owing to lower operating costs.

Halving the discount rate leads to a 33% increase in the total cost of odorants 1 and 2 whereas the corresponding figure for odorant 5 is only 10%. Similarly, a 50% increase in discount rate leads to a 20% decrease in total costs for odorants 1 and 2 and a 6% decrease for odorant 5.

Figure 13 Sensitivity to separator capex in scenario 2

Figure 14 Sensitivity to discount rate in scenario 3

3.6 Limitations

There are several limitations to the analysis which mean that the outputs should be treated with some caution. These include but are not limited to the following

- Data availability – the data obtained were incomplete in some areas and engineering assumptions had to be included where data were not available. For example, w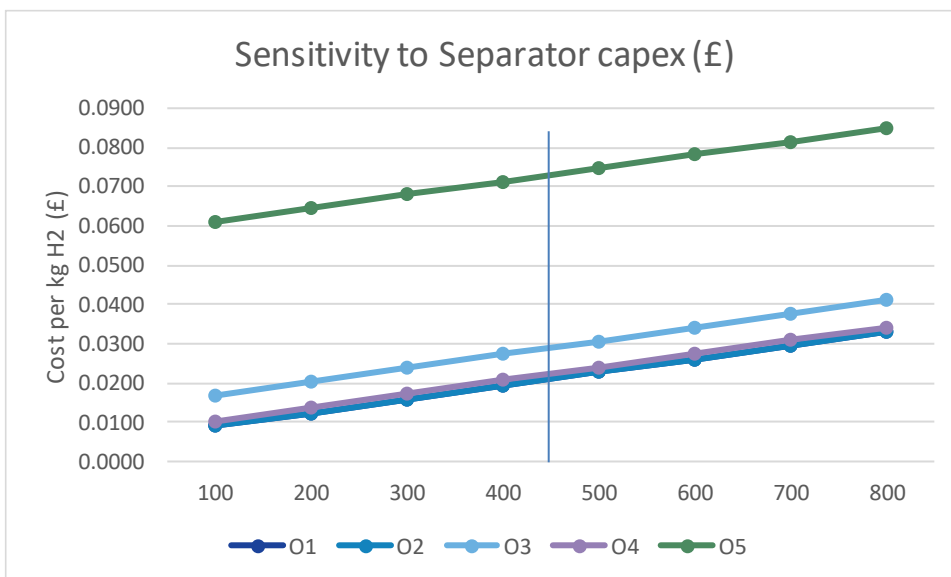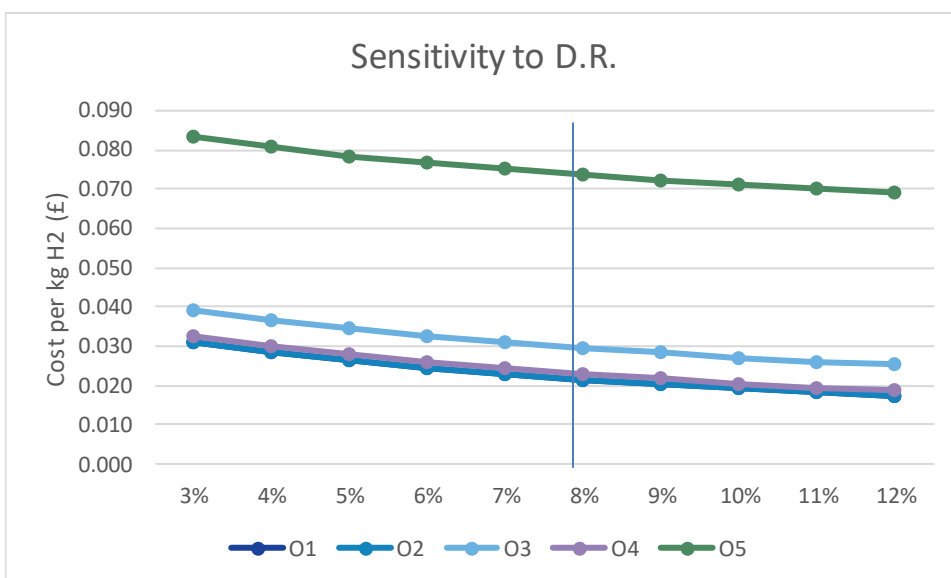hile data on the capital cost of the NG injector systems was obtained, data on energy consumption was not. Similarly, we were unable to obtain cost data on the non-sulphur containing odorants and therefore estimated their cost to be similar to the sulphur containing ones.
- Changes in costs from scaling up not fully incorporated – we costed the system based on the parameters of the small-scale H100 trial and the effects of scaling up to a much larger system could not be fully incorporated in the per kg hydrogen costs. Differences could include aspects such as different utilisation factors for capital equipment and possible volume discounts on odorants. Where possible we have used sensitivity analysis to assess the impact of changes to these parameters.
- Limited data provided on specific hydrogen-related equipment – we were unable to obtain any data on specific hydrogen injector equipment. In the absence of these data we assumed that the systems for hydrogen and natural gas would be identical. We believe this to be a reasonable assumption but have been unable to confirm this. We were able to obtain some data relating to one type of separator for removal of odorants but other types of system may ultimately be used. It should be noted that the data on the membrane separator is rather speculative since these are not yet in common use.
- Fuel cell degradation data from non-sulphur odorants inconclusive – critically, the data from the FC degradation tests proved inconclusive and did not allow any estimate of impact on lifetime or maintenance costs to be calculated. However, it is our view that at present PEMFC manufacturers are unlikely to relax their purity requirements and as a result it will remain essential to separate out odorants before hydrogen is used in fuel cells.
- Data on gas flow profiles was limited – the assumptions used in relation to gas throughput and profile could have an impact on the results.

4 Conclusions and recommendations

Based on the results described in Sections 3.2 to 3.5 and notwithstanding the limitations discussed in Section 3.6, we draw the following conclusions:

- The use of odorant 1 would likely be the most cost-effective solution for a 100% hydrogen network, irrespective of whether boilers or fuel cells are connected to the system, given our assumption that all odorants would have to be removed before use in fuel cells. If boilers only are connected to the network the net cost is less than 1 penny per kg of hydrogen or 0.05% of our assumed delivered hydrogen price (£6/kg). Not only is the cost lower than for other odorants, NB has the merit of being the incumbent odorant in the UK and may allow the re-use of existing equipment.

- If further testing can show that odorant 4 causes no degradation of PEM fuel cells and FC manufacturers accept a lower hydrogen purity than is currently demanded, then assuming, a) even a very small penetration of fuel cells on the network (>1%) and b) that odorant 4 is similar in cost to NB, then odorant 4 becomes the preferred solution.

- Based on a relatively low penetration of fuel cells on the system (20%), the additional cost per kg of hydrogen for odorant 1 in absolute terms (~2 pence) and as a percentage of our assumed delivered hydrogen cost (<0.5%) remains small. However, as the cost of delivered hydrogen declines, as is expected, then this proportion will rise unless similar cost reductions can be made in the cost of separation equipment, for example.

We would make the following recommendations regarding future actions and further analytical work to be carried out.

- Analysis of whether any fundamental redesign of the injection equipment would be required for use with hydrogen should be undertaken in order to either confirm our assumption that costs are equivalent or ensure that an accurate assessment of the delta can be developed.

- More detailed data should be gathered on the costs and performance of existing systems. While the data obtained and sensitivity analysis carried out gives a sound basis for initial indications, obtaining more accurate data should be a priority.

- High level modelling of the configuration of injection equipment and location that would be required for the entire network should be undertaken, giving due consideration to aspects such as redundancy.

- Further tests should be undertaken to ascertain whether or not the non sulphur-containing odorants are detrimental to fuel cells. If this is shown to be the case that these odorants are *not* detrimental, enter into discussions with PEMFC manufacturers regarding a derogation towards the use of these odorants with PEMFC.

Appendix A – Master data and assumptions

Variable Name	Varible Description	Base Value	Unit	Source
O1_Boiler_Eff	Change in boiler efficiency for given odorant	0	N/A	Assumption
O2_Boiler_Eff				
O3_Boiler_Eff				
O4_Boiler_Eff				
O5_Boiler_Eff				
O1_Boiler_Life	Change in boiler lifetime for given odorant	0	Years	Assumption
O2_Boiler_Life				
O3_Boiler_Life				
O4_Boiler_Life				
O5_Boiler_Life				
O1_FC_Eff	Change in FC efficiency for given odorant	0	N/A	
O2_FC_Eff				
O3_FC_Eff				
O4_FC_Eff				
O5_FC_Eff				Assumption

Variable Name	Varible Description	Base Value	Unit	Source
O1_FC_Life	Change in FC lifetime for given odorant	0	Years	Assumption
O2_FC_Life				
O3_FC_Life				
O4_FC_Life				
O5_FC_Life				
O1_Pipe_Life	Change in pipeline lifetime for given odorant	0	Years	Assumption
O2_Pipe_Life				
O3_Pipe_Life				
O4_Pipe_Life				
O5_Pipe_Life				
O1_Flow	Required flow of given odorant	N/A	mg/hour	Calculation
O2_Flow				
O3_Flow				
O4_Flow				
O5_Flow				
OR_Flow				

Variable Name	Varible Description	Base Value	Unit	Source
O1_Inj_Cost	Capital cost of injector for given odorant	231000	£	Thyson
O2_Inj_Cost				
O3_Inj_Cost				
O4_Inj_Cost				
O5_Inj_Cost				
OR_Inj_Cost				
O1_Inj_Energy	Energy consumption for injector for given odorant	1	kW	Assumption
O2_Inj_Energy				
O3_Inj_Energy				
O4_Inj_Energy				
O5_Inj_Energy				
OR_Inj_Energy				
O1_Inj_Num	Required number of injectors for given odorant	1	N/A	Assumption
O2_Inj_Num				
O3_Inj_Num				
O4_Inj_Num				
O5_Inj_Num				
OR_Inj_Num				

Variable Name	Varible Description	Base Value	Unit	Source
O1_Tot_Opex	Total annual opex for given odorant injector and tank	N/A	£	Calculation
O2_Tot_Opex				
O3_Tot_Opex				
O4_Tot_Opex				
O5_Tot_Opex				
OR_Tot_Opex				
O1_Opex	Total opex per kg for given odorant	N/A	£	Calculation
O2_Opex				
O3_Opex				
O4_Opex				
O5_Opex				
O1_Rem_Ann_Capex	Annualised capex of removal equipment for given odorant	N/A	£	Calculation
O2_Rem_Ann_Capex				
O3_Rem_Ann_Capex				
O4_Rem_Ann_Capex				
O5_Rem_Ann_Capex				

Variable Name	Varible Description	Base Value	Unit	Source
O1_Tank_Cost	Capital cost of tank per m3 for given odorant	12174	£	Thyson
O2_Tank_Cost				
O3_Tank_Cost				
O4_Tank_Cost				
O5_Tank_Cost				
OR_Tank_Cost				
O1_Tank_Num	Required number of tanks for given odorant	1	N/A	Assumption
O2_Tank_Num				
O3_Tank_Num				
O4_Tank_Num				
O5_Tank_Num				
OR_Tank_Num				
O1_Tank_Vol	Required tank volume for given odorant	2.3	m3	Thyson
O2_Tank_Vol				
O3_Tank_Vol				
O4_Tank_Vol				
O5_Tank_Vol				
OR_Tank_Vol				

Variable Name	Varible Description	Base Value	Unit	Source
O1_Tot_Ann_Capex	Total annualised capex for given odorant injector and tank	N/A	£	Calculation
O2_Tot_Ann_Capex				
O3_Tot_Ann_Capex				
O4_Tot_Ann_Capex				
O5_Tot_Ann_Capex				
OR_Tot_Ann_Capex				
O1_Conc	Required concentration of odorant 1	6	mg/Nm3	NPL data
O2_Conc	Required concentration of odorant 2	6	mg/Nm3	NPL data
O3_Conc	Required concentration of odorant 3	18	mg/Nm3	NPL data
O4_Conc	Required concentration of odorant 4	8	mg/Nm3	NPL data
O5_Conc	Required concentration of odorant 5	84	mg/Nm3	NPL data
OR_Conc	Required concentration of odorant R	6	mg/Nm3	NPL data
O1_Cost	Cost of odorant 1	62.5	£/kg	Robinsons
O2_Cost	Cost of odorant 2	70.5	£/kg	Robinsons
O3_Cost	Cost of odorant 3	72.5	£/kg	Robinsons
O4_Cost	Cost of odorant 4	70.0	£/kg	Assumption
O5_Cost	Cost of odorant 5	70.0	£/kg	Assumption
OR_Cost	Cost of odorant R	62.5	£/kg	Robinsons

Variable Name	Varible Description	Base Value	Unit	Source
Base_Annuity	Baseline annualisation factor used to calculate annualised capex	12	N/A	Calculation
Base_Life	Baseline equipment lifetime used to calculate annualisation factor	15	years	Assumption
Boiler_Capex	Capital cost of hydrogen boiler	1500	£	Internal sources
Boiler_Eff	Boiler efficiency	85	%	Based on current boilers
Boiler_Output	Boiler peak output	25	kW	Based on current boilers
Discount_Rate	Discount rate to be applied when caculating the annualisation factor	8	%	Assumption
FC_Capex	Capital cost of hydrogen fuel cell	7000	£	Internal sources
FC_Eff	Fuel cell efficiency	90	%	Assumption
FC_Output	Fuel cell peak output	1.5	kW	Assumption
Separation_Initial_Capex	Upfront capital cost of separator	467	£/unit	Element 1
Separator_Replacement_Capex	Cost of replacing seprator every 5 years (2 replacements required)	233	£/unit	
Separation_Capex	Total capital cost of separator equipment per unit	734	£/unit	
Filter_Comp_Power	Power consumption of compressor for separator	0.1	kW	Assumption
Elec_Cost	Cost of electricity to power equipment, e.g. compressors	0.08	£	Assumption

Variable Name	Varible Description	Base Value	Unit	Source
H2_Density	Denisty of hydrogen	0.09	g/l	Engineering data sources
H2_HHV	Higher heating value hydrogen	39	kWh/kg	
H2_LHV	Lower heating value hydrogen	33	kWh/kg	
NG_LHV	Lower heating value natural gas	12.03	kWh/Nm3	
H2_Mass	Equivalent throughput of hydrogen in energy terms for 1000 properties (by mass)	N/A	kg	Calculation
H2_Vol	Equivalent throughput of hydrogen in energy terms for 1000 properties (by volume)	N/A	kg	Calculation
NG_Energy	Annual natural gas energy demand for typical property	13000	kWh/annum	SGN
Peak_Energy_Load	Peak gas energy demand per property	N/A	kW	Calculation
NG_Vol	Annual natural gas demand for 1000 properties (by volume)	N/A	Nm3/annum	Calculation
Num_Prop	Number of properties running on hydrogen	1000	N/A	SGN