ODORISATION OF NATURAL GAS/HYDROGEN MIXTURES AND PURE HYDROGEN

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ABOUT MARCOGAZ

Founded in 1968, MARCOGAZ represents 29 member organisations from 20 countries. Its mission encompasses monitoring and policy advisory activities related to the European technical regulation, standardisation and certification with respect to safety and integrity of gas systems and equipment, rational use of energy as well as environment, health and safety issues. It is registered in Brussels under number BE0877 785 464.

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Contents

1. Introduction

This document was prepared by MARCOGAZ to present what is the available information on odorisation of hydrogen and natural gas (H_2-NG) mixtures and pure hydrogen. The aim is to help defining what are the most important data to be considered when a gas containing hydrogen must be odorised.

The document is divided into a first part dealing with the theoretical interactions between hydrogen and odorants, and following parts on available data on the topic. In the conclusions, some considerations are presented.

2. Theoretical interactions between hydrogen and odorants

Hydrogen was one of the major components of the town gas (cracking treatment produced around 10-20% of hydrogen, while reforming produced up to 60%). In this case however, odorisation wasn't required because of the self-odour of the town gas.

The addition of hydrogen modifies the natural gas composition and – consequently – the physical properties, so a question could be raised if odorisation is affected by these changes. Also pure hydrogen should be odorised for domestic and other uses.

The effects of hydrogen on odorisation can be investigated through different potential impacts:

- Possibility of chemical reactions between hydrogen and odorants,
- Physical effects in the grid,
- Possibility of odorant masking by hydrogen

2.1. Possible chemical reactions between hydrogen and odorants

The information listed below was obtained from the gas odorant suppliers. More information is given in Annex A.

Sulfur odorants are, from the chemical point of view, reduced compounds, so a reaction with hydrogen is not expected. Usually, problems with odorants are produced by oxidation (more with mercaptans than sulphides), mainly in the presence of iron oxides. The common reaction of hydrogen with organic compounds is hydrogenation, which typically is the addition of pairs of hydrogen atoms to an unsaturated bond. Sulfur-based odorants (like THT, mercaptans) are all saturated and, therefore no reaction with elemental hydrogen seems to be likely at the conditions typically found in the gas distribution systems.

Sulfur-free odorants (such as acrylates) exhibit a C=C double bond which makes them prone to addition reactions. Addition of hydrogen however requires a metal catalyst with an active surface. Nevertheless, it is known that in steel pipelines corrosions products and solid deposits may contain some pyrophoric iron, which exhibits an extremely reactive surface due to its fine granularity. These deposits may be able to catalyze an electrophilic addition of hydrogen to the C=C double bond. This may lead to depletion of the odorant as a consequence of a reaction. Although it considered unlikely, it is theoretically possible.

2.2. Physical effect of hydrogen addition in natural gas

2.2.1. Density and vapour pressure

Care must be taken in the choice of the odorant if the amount of hydrogen in the H_2-NG mixture affects significantly the density and vapour pressure of the gas. If the gas density is reduced, the odorant, which is liquid, should be chosen according to the properties of the H_2-NG mixture. Odorants with lower density and higher vapour pressure could better fit for higher amounts of hydrogen in the H_2-NG mixture. Caution should also be taken when the odorant itself is a blend, due to the possible differences in the physical properties of the components of the blend.

2.2.2. Lower Explosion Limits (LEL) of H_2–NG mixtures

Gas odorisation is, in most countries, a legal or regulatory requirement that specifies that natural gas in air has to be readily detectable by odor at a concentration of 20-25 % of the LEL (Lower Explosion Limits).

Hydrogen and natural gas have almost similar LEL values, so the LEL of the mixture doesn't change significantly when hydrogen is injected.

Simulations[1] were done to calculate the LEL of mixtures of two natural gases (Russian-type and Algerian-type) at increasing concentrations of hydrogen. The results are given in Figure 1.

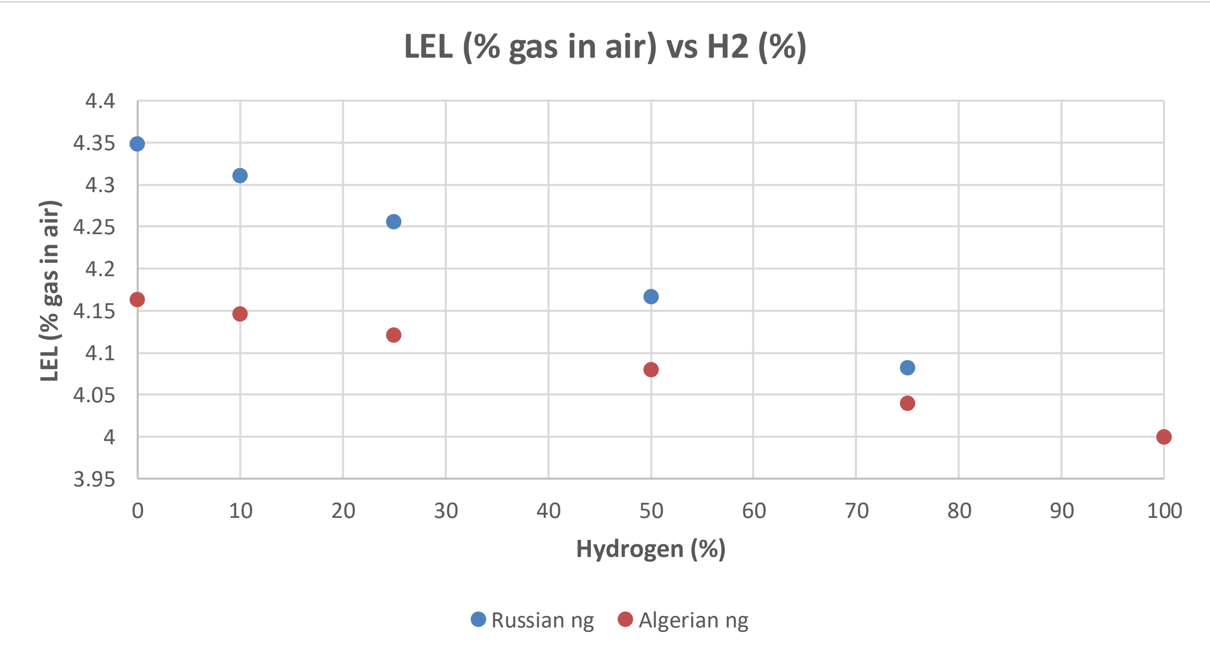

Figure 1: Lower Explosion Limits with different hydrogen concentrations for both Russian and Algerian natural gas. Data calculated in reference to atmospheric conditions: pressure of 101,3 kPa and temperature of 20°C.

[1] Using the method in Schroeder V. "Calculation of flammability and lower flammability limits of gas mixtures for classification purposes" (BAM Berlin, 09-09-2016) and using the values of Li and Kk from EN ISO 10156:2010,

2.3. Odorant masking by hydrogen in H_2–NG mixtures

No evidence of masking effects are available up to now.

2.4. Measurement of odorant in H_2–NG mixtures

Although no problems were reported with gas chromatographs, odorant measurement with chemical sensors could be influenced by hydrogen.

3. Preliminary works

The Final Report of CEN/CENELEC Sector Forum Energy Management / Working Group Hydrogen (2016) deals, in a dedicated chapter, about odorisation of hydrogen injected into natural gas. The final report recommends "*the standardization in order to harmonize the performance indicators for odorants used for H_2-NG*". Two standards are to be considered: ISO TR 16922:2013, which specifies the principles for the odorisation technique and the control of odorisation of natural gas, and ISO 13734:2013, which specifies general requirements for odorants and the physical and chemical properties of commonly used odorants[2]. Odorisation is recalled in other chapters of the same document. It is written: "*Also performance tests on the propagation of smell depending on hydrogen concentrations for new odorants are recommended in the near term and should be addressed before 10 vol% is injected into the natural gas grid.*" It is also mentioned that "*Performance tests to determine the suitability of odorants for different H_2-NG mixtures are recommended in the near term*". Another proposal is to "*investigate the propagation of smell for new odorants in presence of hydrogen*".

GERG identified in its Hydrogen Research Roadmap gaps in the use of hydrogen in the gas grid. Table 1 gives an overview of the gaps related to odorisation:

#	Research topic	Description	Priority
1	**Assess existing odorants compatibility with various H_2 %.**	Evaluate current odorants used in European gas networks (THT, TBM, DMS…), as well as sulfur-free odorants (Gasodor S-Free, 2-Hexyne…) to determine best odorant for H_2 and H_2-NG blends, constrained by factors such as possible chemical reactions, end-use limitations (fuel cells), impact of trace components, public perception, etc. Comparison properties among odorants may include olfactory power, low boiling point,, low toxicity, etc. Also, hydrogen properties must be taken into account for odorant selection, especially flammability and detonation limits, auto-ignition temperature, diffusion in air, etc.	**H**
2	**Study odorants for 100% H_2 and removal techniques for end-use**	Some large users need high purity H_2, (sulfur-free), the choice of a new odorant will need to be done also according to a removal method. It is important to anticipate the	**H**

[2] The ISO TC 193 / WG 5 "Odorization" is in charge to review the current ISO standards.

#	Research topic	Description	Priority
	applications requiring pure H_2.	odorant selection considering first particular end-uses such as fuel-cells, in which sulfur poisons catalysts (filter-some fuel cells are not sensible to sulfur but probably more expensive). Hence, certain removal techniques as well as H_2 identification methods shall be recommended for this type of applications.	
3	**Study if the possible stratification phenomenon in H_2-NG may cause an impact on odorisation.**	Evaluate if during the eventual occurrence of fluids stratification in H_2-NG admixtures, the impact on odorisation would be significant for leak detection. In summer no consumption (static stratification), but both static and dynamic approaches shall be considered.	M
4	**Assess diffusion rate of hydrogen in a leak, versus odorant.**	Evaluate if leak rates for CH_4, H_2-NG & H_2 differ significantly in comparison to the odorant, considering the diffusion rate. It may be useful to distinguish between underground and above-ground leaks, and also to verify possible reactions between the odorant and the soil, depending on the type of odorant.	M
5	**Develop new odorants for H_2-NG/H_2**	Due to the expected growth of hydrogen presence in the European gas networks, for safety reasons, it may be necessary to develop an odorant that complies with some critical conditions including smell, water insolubility, chemical & physical characteristics, end-use applications, impact on steel & other materials properties and public perception. This, only if concluded that odorants currently in use are not compatible or not sufficiently reliable for H_2 leakage detection.	M
6	**Assess the occurrence of odour fading, due to trace components.**	Odour fading may occur for several reasons such as gas quality problems causing masking phenomena and it is important to evaluate if certain trace components may cause these problems, mainly depending on the H_2 source of production. Hydrogen produced by electrolysis may have negligible trace components compared to gasification processes.	M

Table 1: Odorisation related gaps for the use of hydrogen in the GERG Hydrogen Research Roadmap.

4. Experimental tests

4.1. GTS and NN - The Netherlands

During 2019-2020, a research was organized by Gasunie Transport Services (GTS) and Netbeheer Nederland (NN) in order to investigate if increasing hydrogen concentrations can affect the effectiveness of odorisation. DNV GL and SGS Nederland prepared 12 different mixtures of Groningen natural gas (L-gas) at four different concentrations of Hydrogen (0%, 15%, 85% and 100%) and three different odorants: THT (18 mg/m^3), Spotleak 1001® (TBM+DMS 80:20) (6 mg/m^3) and Gasodor ® S-Free (10 mg/m^3).

The different samples were anonymously assessed by a panel of smellers of the Odor Laboratory Bureau Blauw B.V using NEN-EN 13725 "Determination of odor concentration by dynamic olfactometry". It was concluded that mixtures of natural gas and hydrogen and pure hydrogen can be sufficiently odorised with the tested odorants.

No significant effects caused by hydrogen addition were found.

4.2. HY4HEAT - UK

In October 2019, Hy4Heat published a report on "Hydrogen Odorant" (Project Closure Report - Hydrogen Odorant and Leak Detection - Part 1 - Hydrogen Odorant", from SGN), the aim of which was to identify a suitable odorant for use in a 100% hydrogen gas grid for domestic use such as boilers and cookers.

The research involved a selection of five odorants to be tested about the effects of the mixtures on pipeline (metal and plastic), appliances (a hydrogen boiler provided by Worcester Bosch) and PEM fuel cells. For the olfactory test, each odorant was evaluated by 6 panelists. The odorants considered are given in Table 2Table 2:

	Odorant name (including alternative names)	**Compound**	**Rationale**
1	Odorant NB, NB	78% 2-methyl-propanethiol, 22% dimethyl Sulphide	Primary odorant used by Scotia Gas Network 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

Table 2: Details of the five odorants considered in the HY4HEAT project.

The results of the study (green: suitable, red: not suitable, orange: to be more investigated) are given in Table 3:

	Odorant NB	Standby odorant 2	Odorant THT	GASODOR-SFREE	5-ethylidene-2-norbornene
Health/environment	[green]	[green]	[green]	[green]	[green]
Olfactory	[green]	[green]	[green]	[green]	[orange]
Pipeline	[green]	[green]	[green]	[green]	[green]
Flame boiler	[green]	[green]	[green]	[green]	[green]
Fuel cell	[red]	[orange]	[red]	[orange]	[orange]
Economic (*)	[green]	[orange]	[orange]	[orange]	[orange]

Table 3: Results of five odorant experiment in the HY4HEAT project.

(*) Please note that the economic evaluation is referred to UK conditions and cannot be considered applicable as it is to all Europe.

All the odorants were judged suitable for use in a 100% hydrogen gas grid for combustion applications, but further research would be required if the intention fo the grid is to supply hydrogen to stationery fuel cells or fuel cell vehicles.

The olfactory testing suitability was based on odour concentration (how easily the odorant could be detected), the intensity (on the Sales scale) and character (whether it would be distinguishable from other possible odours such as food). All odorants met the testing criteria for odour concentration and intensity. All odorants except 5-ethylidene-2-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-2-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.

4.3. PRCI state of the art on hydrogen

In this study by the Pipeline Research Council International (PRCI), done with the overall goal to develop a concrete path forward to define the necessary projects that need to be completed for companies to safely and reliably inject hydrogen into their pipelines at certain blend levels, there is the following table (Table 4) regarding odorisation:

Topic	**Key results, knowledge is available**	**Gaps, ongoing research or needs further investigation**
Odorants	• At this time, there is no known odorant suitable for hydrogen that is light enough to "travel with" hydrogen at an equal dispersion rate. • Existing projects for hydrogen blending in natural gas, up to 20%, generally	• Evaluation of typical odorants for natural gas and their effectiveness under situations of hydrogen blending at various blend percentages, for practical situations such as pipeline leaks and leaks in buildings where hydrogen may separate from the natural gas and odorant.

Topic	Key results, knowledge is available	Gaps, ongoing research or needs further investigation
	use the standard odorisation for natural gas. • A recent study of common odorants THT, Spot-leak® 1001, and Gasodor® S-Free concluded that all odorants were detectable in a range of hydrogen blending in natural gas (from 0% to 100%), however the experimental set up did not allow for consideration of hydrogen separation from the natural gas. • (NOTE: the last sentence is referred to the work described in chapter 4.2 of the present document).	• Particularly for situations of pipeline leaks, the stratification of hydrogen from natural gas, and therefore from the odorant, needs to be better understood to advise safety protocols during leaks and repairs. It would be useful to be able to evaluate a timescale for gas separation/concentration gradient at ambient pressure (i.e., does it take hours/days for hydrogen to separate from the natural gas and odorant?). • Assessment of alternative options for identifying leaks and specifically hydrogen gas when blending hydrogen at higher percentages. • Conflicting data exists regarding the effectiveness of common natural gas odorants for detecting pure hydrogen; further investigation is required to assess if hydrogen separated from natural gas following leakage could be effectively identified.

Table 4: PRCI state of the art on hydrogen regarding odorisation

4.4. HYDROGEN 100 project – UK.

The Hydrogen 100 project SGN (Scotia Gas Networks Limited) aims to deliver 100% hydrogen to 300 homes in the UK via a purpose-built distribution network.

A second study, described in the paper "A comparative study of odorants for gas escape detection of natural gas and hydrogen" (Julien Mouli-Castillo, Georgina Orr, James Thomas, Nikhil Hardy, Mark Crowther, R. Stuart Haszeldine, Mark Wheeldon, Angus McIntosh), available online from 20 February 2021, refers of the tests performed at the KIWA laboratories, to study the physical and olfactory properties of high purity hydrogen and odorant mixtures. Three of the four odorants of the first study were tested during 2021:

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

The concentrations of the odorants were 500 ppm, 1000 ppm and 10.000 ppm, both in hydrogen and natural gas; the gas was considered detectable when 50% or more of the trial participants detected a smell on a given sample line.
Firstly, the work provides evidence that odorants currently used within natural gas have similar effectiveness in allowing escape detections as when used with hydrogen. Secondly, the study shows that small escapes of hydrogen are detectable in a comparable way to a natural gas escape in an equivalent room volume. Both studies conclude that odorant in hydrogen will induce an equivalent olfactory response to odorant in natural gas. These conclusions can be considered robust as they were demonstrated by two different methodologies using very different approaches.

In particular, the results indicated that stratification of the gases within an enclosure 3 m high does not negatively affect the detection potential of a gas escape. Both hydrogen and methane escapes can be detected at equivalent Gas in Air (GIA) concentrations and both at the required value of 1% GIA.
The study found that odorants appeared to remain with the hydrogen gas as it moves through an enclosed space. In literature it is reported that the molecular weight and dispersion properties of hydrogen, relative to odorant compounds, were likely to lead to the odorant not remaining within the gas stream in a stagnant environment; however, they also suggested that in a domestic dwelling, ventilation could be sufficient to drive dispersion and to keep the odorant mixed with the gas stream. The finding of the study (mimicking a real new dwelling environment with natural ventilation) supports this for hydrogen, natural gas and methane.

4.5. INiG—PIB (Poland)

The INiG—PIB's project studies the stability of the THT concentration in gaseous mixtures with the addition of hydrogen, taking into account the conditions of the Polish gas network. The results of the research (presented in the paper "Studies of the Impact of Hydrogen on the Stability of Gaseous Mixtures of THT", Authors: Anna Huszal and Jacek Jaworski - Energies 2020, 13, 6441) are a basis for forecasting the impact of hydrogen on the quality of odorisation of gas using THT.

The mixtures of methane and hydrogen, as well as methane-rich natural gas and hydrogen, used as reference gases for tests were made up of the following compositions:

- methane with the addition of hydrogen with an amount of 8% (V/V),
- methane with the addition of hydrogen with an amount of 10% (V/V),
- methane with the addition of hydrogen with an amount of 15% (V/V),
- methane-rich natural gas of group 2E with a hydrogen content of 2% (V/V),
- methane-rich natural gas of group 2E with a hydrogen content of 15% (V/V).

The tests were limited to just THT, as this was the one used most frequently in European practice and the only one used in Poland; the THT concentration should correspond to its average values in the distribution network, i.e., fall within a range of 15.0–30.0 mg/m3 (approx. 4.0–8.0 ppm).

Compositions of tested gaseous mixtures:

1) M/H8: THT 92% Methane + 8% H_2 (V/V) + 5.07 ppm THT
2) M/H10: THT 90% Methane + 10% H_2 (V/V) + 7.44 ppm THT
3) M/H15: THT 85% Methane + 15% H_2 (V/V) + 6.70 ppm THT
4) 2E/H2: THT 98% Natural gas of group 2E + 2% H_2 (V/V) + 5.23 ppm THT
5) 2E/H15: THT 85% Natural gas of group 2E + 15% H_2 V/V) + 7.41 ppm THT

The mixtures, prepared by means of static volumetric techniques, were contained in 10 L aluminum pressure bottles. The tests involved reference mixtures of N_2 + THT, considered as a point of reference for the stability of mixtures of THT with gases containing the addition of hydrogen. The studied time interval was 126 days.

The results of the tests confirm that a hydrogen content up to 15% in gas will not interact with THT; these results determine the probable lack of a need to change the odorant for mixtures of natural gas with hydrogen.

Such promising results of preliminary tests point to a need to test the long-term stability of THT mixtures, taking into account changes in the parameters when performing the experiment (pressure and temperature). Based on previous experience, it can be concluded that it is highly likely that THT mixtures with the studied compositions will remain stable even for several years, since most of the reactive components begin to exhibit losses immediately after the preparation of the mixture.

4.6. HyDelta WP2 on odorisation

Work Package 2 of HyDelta was meant to fill some of the knowledge gaps in order to pave the way for the introduction of a hydrogen odorant. Two candidate odorants already have been chosen:

- Tetrahydrothiophene (THT): sulphur containing odorant, used in Dutch natural gas.
- Gasodor© S-Free: sulphur free alternative. Have been used in the past in natural gas.

The research identified new goals and timing are given in Table 5:

Project	Goal	Deadline
D2.1	Choice for a sulphur free odorant	11-10-2021
D2.2	Influence of sulphur containing odorant on end use appliances	25-01-2022
D2.3	Stability of odorants in hydrogen	29-04-2022
D2.4	Report on the risks of not odorising hydrogen (to be published alongside the end of project summary)	tbd
D2.5	Report with advice over odorising hydrogen including a possible choice for a defined type of odorant and its dosing	tbd

Table 5: Overview of research projects in WP2 of HyDelta.

The study has shown that no insurmountable problems are to be expected for combustion equipment such as central heating and hot water boilers, kitchen appliances, ornamental fireplaces, outdoor heaters and patio heaters and gas engines when using hydrogen that has been odorised with sulfur-containing odorant, such as THT.

While these applications are relatively robust for low concentrations of sulfur (<14,5 mg $S/m^3(n)$) in hydrogen, fuel cells are very sensitive to these impurities. The presence of sulfur in hydrogen leads to irreversible damage to the fuel cell[3]. This is an accumulating process, which already occurs at sulfur concentrations of 1 ppm (1,4 mg $S/m^3(n)$).

The development of hydrogen-driven gas turbines is still in full swing, little is therefore currently known about the hydrogen specification ultimately required for gas turbines. In principle, gas turbines fall under ISO 14687 gradation B, with a specified sulfur concentration of 10 molppm corresponding to approximately 14 mg $S/m^3(n)$. This concentration corresponds to the maximum specification that currently applies to natural gas distributed in the Netherlands. It has been known from the past that natural gas-fired turbines are suitable for this sulfur load. It is up to the suppliers to make the gas turbines still to be developed suitable for this sulfur load.

For feedstock applications, where the hydrogen is used directly in the production process, impurities such as sulfur are highly relevant. These processes are so specific that no statements can be made in general terms about the maximum permissible sulfur content in the hydrogen, but it is expected, however, that additional cleaning will have to be applied, as is now also the case for odorised natural gas. It should be noted that almost all feedstock processes are connected to the unodorised high-pressure transport system (HTL). It is expected that, in accordance with the current HTL network in The Netherlands, the hydrogen backbone will also not be odorised and the sulfur impact will not be increased. The impact of sulphur-containing hydrogen will therefore not be an issue for such applications.

4.6.1. Report D2.3 on Stability of odorants in hydrogen (June 2022):

The Report D2.3 refers to three different activities:

- The candidate odorants, at different concentrations of hydrogen, were tested for chemical stability in an atmosphere of 100 bar hydrogen over a three-month test period by gas chromatographic analysis. The influence of materials such as the cylinder wall and the pipeline material has not been investigated and falls outside the scope.
- A literature study on how an odorant-hydrogen mixture spreads in the air.
- The diffusion of a mixture of odorant and hydrogen in the soil, by a simulated gas leak, measuring the gas composition when the gas escapes from the soil with a gas chromatograph.

The stability tests show that the three odorants THT, Gasodor® S-Free and 2-hexyn are all stable for three months in a 100 bar hydrogen mixture for three distinct levels of the odorant, allowing them to exert their effect for a longer period of time.
From literature experiments on a simulated gas leak consisting of natural gas, hydrogen or a mixture of hydrogen and natural gas, it appears that the gas mixtures behave like a cloud and that no spontaneous separation of gases from the cloud takes place. This behavior is also supported by theoretical considerations. The difference between distribution in air of natural gas and hydrogen is negligible.
In the case of an odorant/hydrogen gas leak, it also behaves as one gas cloud, and no separation of the odorant and hydrogen takes place. It is possible that the concentration in space is not the same everywhere due to stratification, but this effect also applies to natural gas. Regarding the distribution of gas in a room and the smell of a gas leak, odorisation of hydrogen is just as effective as odorisation of natural gas.

[3] For more information about fuel cells and Hydrogen, see the web site of the PACE project (see bibliography for link), which has the scope of deploying a competitive European fuel cell micro-cogeneration market.

With regard to the behaviour of an odorant in hydrogen in the soil, which is important for examining gas leak behaviour, it appears that THT in a clean sandy soil is detected later at the surface than THT in natural gas. It is recommended to repeat these measurements in more humus-rich soil, so that the practical conditions are more closely approximated.

4.7. Pre-normative tests performed in Italy

In Italy, the Ministerial Decree of 3 June 2022 allows the distribution of up to 2% of Hydrogen. In order to develop adequate standards for the new allowed gas composition, two distribution companies performed tests to see if the presence of Hydrogen will affect the odorisation, using the odorants in use in Italy, at the minimum concentration stated for natural gas (THT at 32 mg/m^3 and TBM (as major component of the mixture with IPM and NPM) at 9,3 mg/m^3).

Italgas Reti performed tests with methane and 20 % of hydrogen, in presence of DMS, a sulphur compound that is present in some of the natural gas that are extracted in Italy and can give interferences with THT. The results confirms that there is no need to change odorants or modify the minimum concentrations. The presence of DMS is due to perform the test at the same conditions in which they were performed for the emission of the national standard UNI 7133-2.

Hera performed test with natural gas with 30% of hydrogen added, with the two odorants in use; also, these results confirm that there is no need to change odorisation process.
The results will be included into the new revision of the national standard UNI 7133-2 “Gas odorisation for domestic and similar uses – Part 2: requirements, check and management”, under discussion.

5. Field tests

These data were collected by MARCOGAZ members, based on available information at the time of the report was made.

5.1. Hydrogen injection into natural gas at Maximum Operating Pressure (MOP) ≤ 16 bar

5.1.1. France

An experimental project (called GRHYD, coordinated by ENGIE from 2014 until 2020) is injecting progressively hydrogen, up to 20% in concentration, into natural gas in a local, new and dedicated odorised natural gas grid. The decision is to not odorise hydrogen, because the dilution factor used (even the maximum one) and the concentration of the THT of the mixed natural gas are still in adequacy with the technical requirement of the distribution operators. A µGC (micro-Gas Chromatograph) will measure on-line the concentration of THT before the injection of hydrogen.

5.1.2. Germany

Several injections of hydrogen (with a concentration up to 2%) into natural gas grids are operated, but, so far, no effect of the hydrogen onto the odorisation has been reported:

- Near Hamburg, hydrogen is injected into the grid of HanseGas which is odorised with the odorant mercaptan mixture based on TBM (Tert-butyl-Mercaptan). No report on odorisation problems raised, too.
- In Frankfurt, hydrogen is injected into the local grid, which is odorised with a mercaptan mixture based on TBM. In that grid, there were severe problems with the odorisation, but those could be identified not being caused by the hydrogen injection. The source of the problem was two biogas plants feeding their biomethane into the gas grid. The biomethane was conditioned with LPG to achieve the Wobbe-index of the natural gas, and the trouble came from interferences with the odorant in the LPG.
- There are some more injections of hydrogen in Germany, but at the moment there is no information about that.
- At Dortmund from 2022, distribution of pure hydrogen started in a local grid; the gas is odorised with THT with good results, but there was the necessity to increase the concentration of the odorant of about 20%, stated by olfactory tests, probably due to the higher speed of hydrogen, which needs a higher odorant concentration for flux saturation.

The German National Committee on odorisation gives the following indications:

- To odorise natural gas/hydrogen mixtures, the odorants specified in (EN) ISO 13734 will suffice.
- To odorise "pure" hydrogen grids, there will only be the need for odorisation if the hydrogen replaces the natural gas delivered to "ordinary" customers. So far, all existing or future pro-

jected hydrogen grids for the chemical or other industrial plants e.g. power stations, are foreseen without the need for odorisation. However, there may be grids reaching normal "tariff" customers in some years and given the option that also some fuel cells will be connected, odorants without sulphur may need to be developed and adapted.

- Hydrogen odorants may be demanded in the near future, probably raising the need for standardization.

5.1.3. Italy

Up to now in Italy there is no injection of hydrogen into the natural gas grids, so there is no direct experience on a possible interference between odorant and hydrogen. Anyway, there were experiences with odorisation of manufactured gases. A confidential study dated 1983 refers on rhino-analytical controls of grids distributing natural gas and manufactured gas containing hydrogen, both odorised with mercaptans: no differences were noted.

The composition of manufactured gas was roughly the following:

- Methane: 45 %;
- Hydrogen: 28 %;
- Carbon Monoxide: 8 %;
- Carbon Dioxide: 8 %;
- Oxygen: 2 %;
- Nitrogen: rest.

5.2. Hydrogen injection into natural gas at MOP > 16 bar

5.2.1. The Netherlands

At the moment there is a single part of the grid where refinery gas, containing up to 15% of hydrogen, is odorised with THT at 18 mg/m^3(n). Every 3 weeks the degree of odorisation is measured with a µGC, without any reported failure in odorant concentration. No olfactory test can be performed due to the presence of CO in the gas.

So far, no other data is available on odorisation effect from the injection of hydrogen in gas network at MOP > 16 bar.

5.2.2. France

The Jupiter 1000 project (coordinated by GRTgaz since 2014) is the first industrial demonstrator of Power-to-Gas (P2G) in France with a power rating of 1 MWe for electrolysis and a methanation process with carbon capture. The scope is to convert renewable power surplus into green hydrogen and syngas, injecting it into the gas grid. On the Jupiter 1000 platform, pipelines are made of stainless steel, similar to the transmission network. A maximum 6% of hydrogen will be injected in transmission pipelines containing natural gas. No odorisation addition is performed due to the low level of dilution of hydrogen in natural gas. Also, no control of the level of THT after the hydrogen injection in natural gas are scheduled.

6. Conclusions and actions

No evidence of problems in odorisation after addition of hydrogen to natural gas were found yet, although experiences are small, up to now. The available olfactory results show that the odorisation of natural gas - hydrogen mixtures could be performed with the same odorants and concentrations as for natural gas. Results have demonstrated that an odorant is equally distributed in a leak, both in confined and open space, besides the possibility of separation of natural gas and hydrogen due to the differences in physical properties. Some differences can be found when a leak of odorised gas crosses the soil, where the odorant could be easily adsorbed when mixed in hydrogen (experiences only on THT). This behavior is related to the physical properties of hydrogen, so it could be limited using odorant with the most similar physical properties with hydrogen.

Data are usually related to conditions of distribution grids, so it is not easy to extend the information to higher pressures as common in transmission grids (when odorised), even if the hydrogenation is not expected in the absence of catalysts.

Taking into account what was previously reported, MARCOGAZ suggests to consider a safe concentration of hydrogen in the natural gas – for odorisation with traditional odorants – up to 20% of hydrogen. Pilot projects demonstrate that odorisation of blends up to pure hydrogen using natural gas odorants give promising results, but more evidence is needed, particularly on the amount to be used when taking into account the differences in flow rates. MARCOGAZ is awaiting new data on the topic, as more information is needed regarding the following items:

- Possible effects on odorisation due to differences in physical properties of the mixture of gas and odorant (density, vapour pressure, …), at the actual condition of the distribution and transmission grids.
- Possible chemical reaction between hydrogen and odorant at high pressure condition.
- Influences from possible impurities from hydrogen production.

In particular uses, that can be encouraged in the case of the use of pure hydrogen (for instance fuel cells), the presence of the odorants may have a negative effect. A solution could be the removal of sulfur (and the other poisoning agents) for the sensitive users, by means of filtering. A second possibility will be the use of sulfur free odorants, already available or now under development, which have to be tested for the effectiveness in avoiding the issues with the final utilization by the customers.

In the case of fuel cells for instance, the use of some kind of filter would be needed to remove the odorant (even if sulfur free) due to the high purity hydrogen that is needed for this kind of application.

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8. Annex A: Information on odorants for hydrogen received by odorants producers

Physical data from Producer 1:

Odorant	density at 273K (kg/m^3)	density at 288K (kg/m^3)	vap pressure at 273K (mbar)	vap pressure at 288K (mbar)
THT+ EA (Ethyl Acrylate)	950	910	11	27
THT	1016	1003	5,8	13
TBM+IPM+NPM	825	810	82	169
TBM+MES	828	813	71	152
TBM+DMS (UK+IE)	830	814	114	230
TBM+DMS (CZ)	837	817	140	246
EM	861	844	246	486

Physical data from Producer 2

Name	density at 273K (kg/m^3)	density at 288K (kg/m^3)	vapour pressure at 273K (bara)	vapour pressure at 288K (bara)
THT (SCT)	1015,73	1002,78	0,00554	0,014
TBM-IPM-NPM (SC E)	824,33	810,8	0,00842	0,17
TBM-DMS (SC F20)	830,09	814,36	0,1226	0,23
THT-TBM (SC TB5)	907,83	893,1	0,0406	0,084
EM (SC A)	861,32	844,31	0,246	0,474

Regarding sulphur free odorant based on acrylates, there are no experience concerning the effect of minor concentrations of H_2 (up to 20%). This will have to be tested in further investigations.

On the other side, already in the year 2014, a product was developed which purpose is to be used with pure hydrogen. This new product, however, is not yet being used anywhere in the world, therefore is not yet commercially available and not yet approved.