HyDelta

WP2 – Odorisation of Hydrogen

D2.3 – Stability of odorants in hydrogen

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Executive summary

This report D2.3 is part of HyDelta work package 2 "Odorization of hydrogen" and describes the long-term stability of candidate odorants for hydrogen in a hydrogen gas matrix. Furthermore, the current knowledge about the behaviour of odorant and hydrogen in a soil, compared to the behaviour of odorant and natural gas will be summarized. Also, the current knowledge about possible de-mixing effects of odorant in hydrogen after a gas leakage will be summarised.

Three candidate odorants, all selected in a previous phase, were tested for chemical stability in an atmosphere of 100 bar hydrogen over a three-month test period by gas chromatographic analysis. All odorants THT, Gasodor® S-Free and 2-hexyn, were found to exhibit stable behaviour, allowing them to exert their effect for a longer period of time.

In the case of a gas leak from a mixture of an odorant in hydrogen, it behaves like a singular gas cloud and no separation of the odorant and hydrogen occurs. It is possible that the concentration of the mixture in space is not the same everywhere due to stratification, but this effect also applies to natural gas. With regard to the distribution of gas in a room and the smell of a gas leak, odorization of hydrogen is just as effective as odorization of natural gas.

The behaviour of an odorant in hydrogen in soil, which is important for examining how a gas leak in the soil behaves, will be reported in the final version of this report in mid-2022.

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1. Introduction

The research question that will be answered within this part of the HyDelta program is: is odorant in hydrogen stable in the gas phase or does some form of degradation take place? Furthermore, the question is answered whether a gas mixture of odorant in hydrogen spreads in the same way in the soil or in air as a gas mixture of odorant in natural gas.

The three sub-studies are carried out as follows:

- practical research: stability of odorant in hydrogen: different concentrations of hydrogen are made with the odorants THT, Gasodor® S-Free and 2-hexyne and the composition is determined over time over a period of three months. These odorants were selected in a previous study [10]. The influence of materials such as the cylinder wall and the pipeline material has not been investigated and falls outside the scope.
- literature study: how an odorant-hydrogen mixture spreads in the air: the results of research from the British project H100 [8] and research from the knowledge centre for gas network management are summarized and analysed to determine whether odorant separation occurs in a hydrogen cloud;
- practical research: diffusion of a mixture of odorant and hydrogen in the soil: a gas leak is simulated in which the gas composition when the gas escapes from the soil is measured with a gas chromatograph. The results of research by the knowledge centre for gas network management (Kenniscentrum Gasnetbeheer) are described here.

The section “distribution of a mixture of odorant and hydrogen in the soil” has not yet been completed in March 2022. The results of this latest study will be included in a final version in June 2022. This report version is therefore a preliminary version. The full version will be released in mid-2022.

2. Stability of an odorant in hydrogen

It is important for an odorant that it is chemically stable, because the odorant must not decompose before it is supplied to a connected consumer. This is one of the criteria that apply to the use of an odorant (see deliverable 2.1A).

The reference gases used for the analytical determination and control of the odorant content must also be stable. For reference gas of THT in methane, a validity period of three years is stated for the specified analytical contents after production. Hydrogen is not expected to chemically interact with the odorant at room or ground temperature. It is important to verify this, because this stability has not been studied before.

2.1 Preparation of the mixtures and methods of analysis used

For the preparation of the gas mixtures, use was made of hydrogen of a high purity (minimum 99.999 vol%) to which odorant is added and whereby a mixture with a relatively high concentration is made. The concentration is determined on the basis of the weighed-in weights. This mixture is then diluted with hydrogen and compressed in a suitable cylinder at a pressure of 100 bar. This pressure has been chosen because the possible effect of a reaction of hydrogen with the odorant will be strongest at a high partial pressure of hydrogen. In this case 100 bar is a worst case. The suitability for gas transport networks (for natural gas these have a pressure of 40 or 67 bar) can also be tested. The cylinder wall is passivated with a coating (silanized). The cylinders with gas mixtures were prepared, stored and analysed at a temperature of 20 °C.

To measure the stability, the nominal, minimum and maximum amount of odorant was measured. The nominal value is the value that is regulated in practice. In practice, this value fluctuates due to deviations from the dosed amount with the set amount and adsorption of odorant on the pipe wall. The minimum and maximum values for THT are both recorded in the Ministerial Decree gas quality [4]. If the dosage is too low, there is a risk that a gas can no longer be smelled properly. An overdose is undesirable, partly because this leads to a higher sulphur content in the gas and can change the odour recognition. The nominal value of THT in natural gas is 18 mg/m^3(n), the minimum value is 10 mg/m3(n) and the maximum value is 40 mg/m^3(n). Because the odorant smell is not expected to be influenced by the gas matrix, the same values for the odorant content as in natural gas were used in this test for hydrogen.
For Gasodor® S-Free, the ideal and minimum dosage in Germany is defined in G280-1, namely 14 and 8 mg/m^3(n) [2]. The maximum value has not been set. For the experiments described in this report, the maximum value is derived from the value for best before date.

For the 2-hexyne odorant, the study, described in report D2.1a: "Choice for a sulphur free odorant"[10], compared the odour strength in hydrogen with that of natural gas odorized with THT at the same dilution degree in air. This resulted in a concentration of 15 mg/m^3(n) of 2-hexyne. By analogy with the values of THT, 10 mg/m^3(n) has been used as the minimum content and 35 mg/m^3(n) as the maximum odorant content.

The set values are listed in Table 1.

Table 1: values for the stability tests of odorants in hydrogen

Odorant	Nominal value (mg/m³(n))	Minimum value (mg/m³(n))	Maximum value (mg/m³(n))
THT	18	10	40
Gasodor® S-Free	14	8	32
2-Hexyne	15	10	35

Legend: yellow was created by DNV, green was created by Kiwa, orange was created by both DNV and Kiwa.

To test the stability, the following times for analysing the odorant content have been agreed: 1 day after production, 1 week, 2 weeks, 4 weeks, 2 months and 3 months.

DNV and Kiwa performed the measurements using GC-FID (gas chromatography combined with flame ionization detector).

2.2. Analysis results

Figure 1 shows Kiwa's analysis results of THT in hydrogen. The fluctuation in the results is relatively high. No explanation has been found for this. Because the trend in the fluctuations is the same for each level and there is no systematic decrease over time, the results are all useful.
The maximum value of THT of 40 mg/m³(n) is lower than calculated. Possibly due to a weighing error. For the purpose of this test, which is to demonstrate the chemical stability of the compound, the measurement is still representative.
For comparison, the THT content in natural gas of the so-called “Working Reference Material” (WRM) is included in figure 1. See the yellow line.

Regarding stability, there is no systematic decrease in concentration. The THT mixtures in hydrogen , as well as the THT mixtures in natural gas, may therefore be judged to be chemically stable.

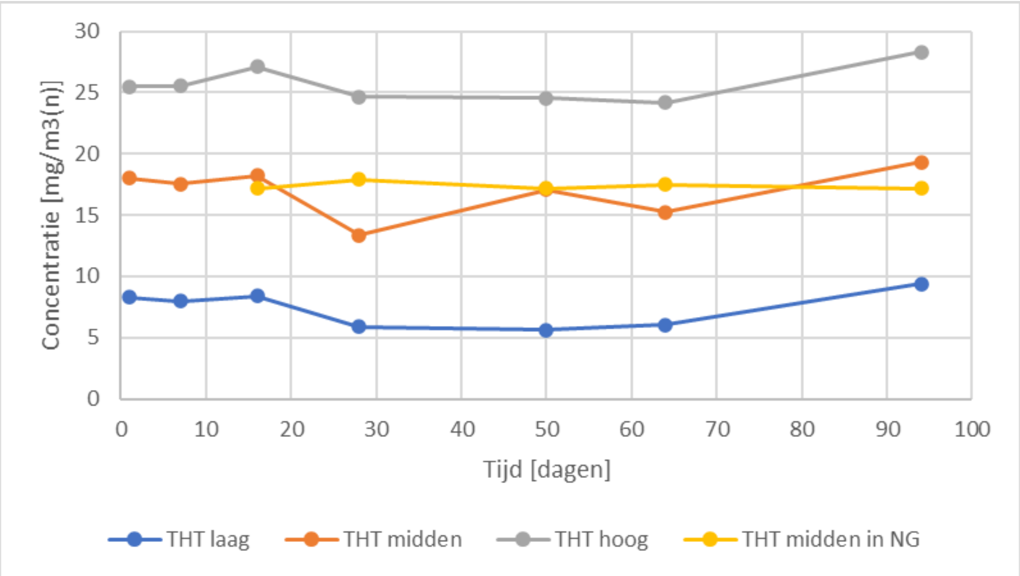

Figure 1: Results Kiwa for THT in hydrogen

Figure 2 shows DNV's results for Gasodor® S-Free. In all cases there are values with a fluctuation of less than 1 mg/m3(n). There is no question of a systematic decrease in concentration. The Gasodor® S-Free mixtures may therefore be assessed as stable.

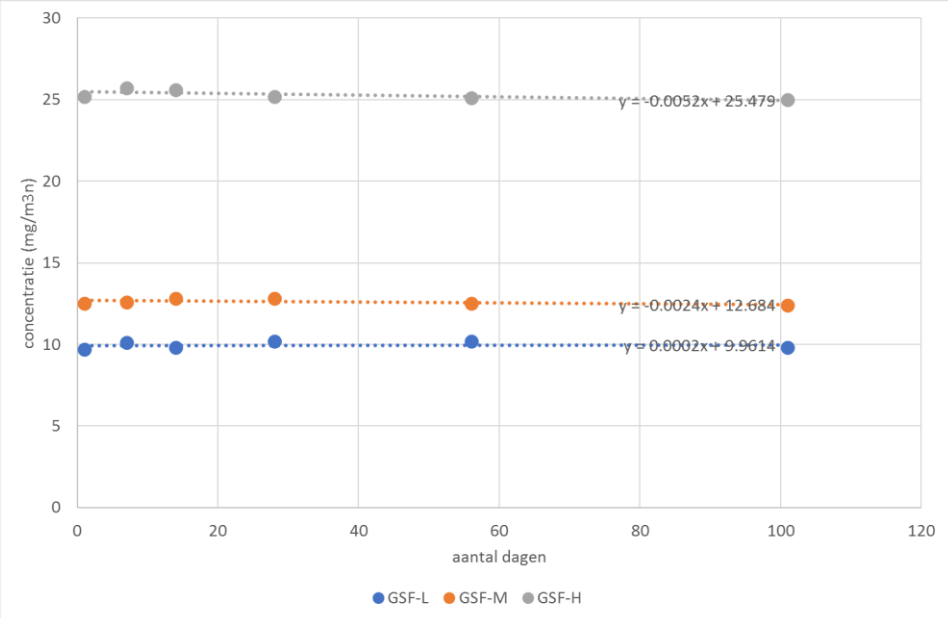

Figure 2: Results from DNV at Gasodor® S-Free in hydrogen (nominal, minimum and maximum value)

Figure 3 shows Kiwa's results for 2-hexyn and Figure 4 those of DNV. In all cases there are values with a fluctuation of less than 1 mg/m^3(n). There is no question of a systematic decrease in concentration. The 2-hexyne mixtures may therefore be judged to be stable.

The measurements of Kiwa and DNV are comparable. The high 2-hexyne value of Kiwa is higher than the target value of 35 (mg/m^3(n)). This is due to a weighing error. For the purpose of the experiment, the exact initial concentration is not relevant as the purpose of the experiment was to verify that the concentration does not decrease over time. There is a very slight fluctuation and there is no systematic decrease in the concentration.

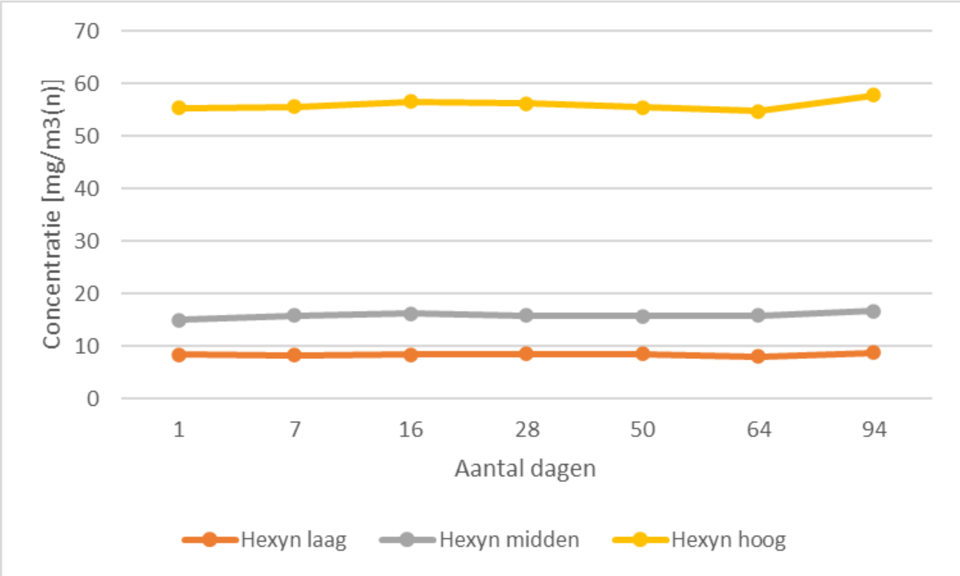

Figure 3: Results Kiwa for 2-hexyne in hydrogen

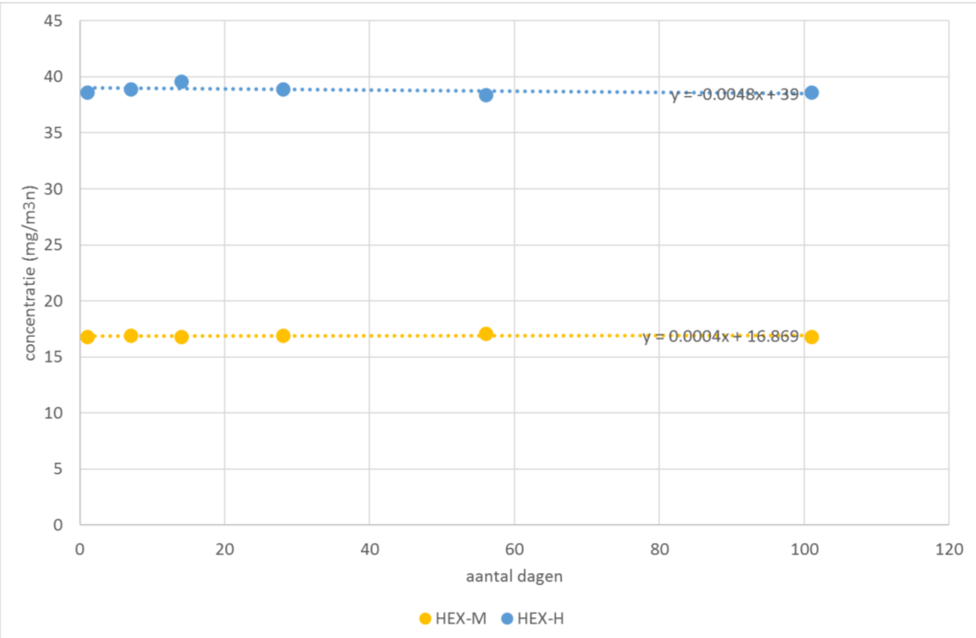

Figure 4: Results DNV for 2-hexyne in hydrogen

2.3 Conclusions and recommendation

The key research question is whether the odorant in odorized hydrogen is stable in the gas phase and whether there is no degradation.

The measurements on three candidate odorants in hydrogen at a hydrogen pressure of 100 bar show that the odorants show no variation in concentration over a period of three months. This means that there is no chemical conversion, such as hydrogenation or decomposition. The trend line of the concentration of THT in hydrogen is comparable to that of THT in natural gas.

Under the chosen conditions (room temperature and 100 bar hydrogen pressure for three months), the three odorants are all stable, making them effective for a longer period of time.

It is recommended to further investigate the stability of an odorant before implementation on, for example, decompression of gas by testing at higher temperatures up to, for example, 100 °C. Hydrogen gas heats up during decompression. The influence of the material has not yet been investigated. Now inert (coated) cylinders have been chosen. Research into the influence of uncoated steel cylinders and aluminium cylinders is therefore recommended.

3. The behaviour of an odorant in a gas cloud

By analysing some recent papers, the current knowledge on the distribution of hydrogen and in particular odorized hydrogen, is described. This is done to check whether the hydrogen may separate from the odorant, which may have consequences for the detection of a gas leak. The publications describe:

- measurements of deliberately introduced gas leaks of various gas mixtures in a house;
- calculations and modelling of a gas leakage of methane and hydrogen in a room;
- experimental measurements of the concentration of odorant and the odour strength in a room where odorized hydrogen is introduced into a room by means of an artificially installed leak.

The studies are summarized and analysed to describe the behaviour of a hydrogen/odorant gas mixture in air.

In order to properly understand the behaviour of the odorant in hydrogen, an explanation is first needed about how hydrogen spreads in a room.

3.1 The behaviour of a hydrogen leakage in a home

A large number of experiments on the leakage of hydrogen in a house have been carried out in the context of the Hyhouse project [8]. A number of leaks have been created on the ground floor of an existing house, whereby the gas concentration is measured in several rooms of the two-storey house at three heights in the room (just above the ground, just below the ceiling and at a middle height of a space).

Leak sizes ranged from 8 to 64 kW per minute. The kW energy unit was chosen because the energy content of the leaking gas is a measure of the impact of a possible ignition. Hydrogen is about 8 times lighter than natural gas. Although the energy content of hydrogen per volume is three times smaller than for natural gas, the leak from a natural gas pipeline will contain about the same amount of energy as a hydrogen leak from a leak hole of the same size. This is because the leakage volume is approximately inversely proportional to the square root of the relative density.

The most important experiences from this research are:

- there is a stratification of the hydrogen concentration on the ground floor of the house, but this also applies to natural gas (see figure 5);
- this layering has disappeared on the first floor of the house (bedroom 1 and 2);
  the concentration of hydrogen in the home depends on the ventilation and tightness of the home. Hydrogen "escapes" from the home more easily, so when comparing the natural gas and hydrogen leaks, it appears that the energy content of the leaked gas in the home is smaller for hydrogen than for natural gas. This effect had already been calculated from simulations, but the measured effect turned out to be slightly stronger than predicted. By making the house increasingly crack-tight, the ventilation of hydrogen from the house became less (see table 2).

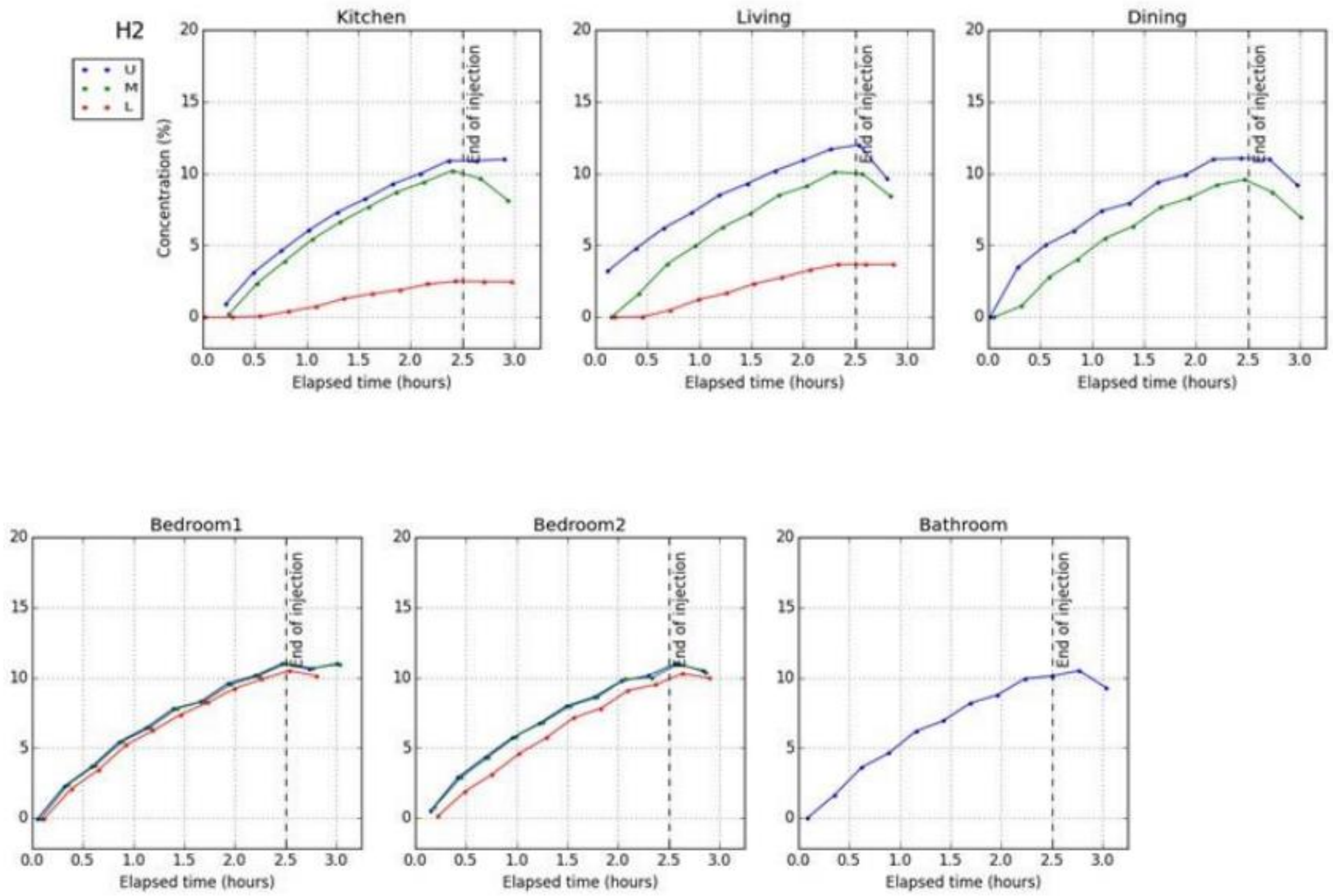

Figure 5: Concentration measured over time of hydrogen at three heights in the event of a gas leak in five different rooms in the test house (U = upper, upper measuring point, M is middle height, L is lowest measuring point, just above the floor)

Table 2: comparison of the concentrations of hydrogen and methane found in leak experiments in Hyhouse

Gas	Start of the project	After applying seals	After even higher sealing degree
H_2 measured	4.3%	7.1%	8.1%
CH_4 measured	3.2%	5.5%	5.5%
Measured ratio H_2/CH_4 in the room	136%	129%	158%
Composition leakage gas : input H_2/CH_4	340%		
Calculated H_2/CH_4 composition measured based on density model	173%		

The Hyhouse study also measured town gas. Town gas has no fixed composition. The composition has been chosen for this experiment as: 50% H_2, 25% CO_2 and 25% CH_4.

This experiment shows that stratification also occurs with town gas that has a density comparable to natural gas for the chosen composition. The individual components H_2, CO_2 and CH_4 follow this stratification as shown in figure 6. The ratios between the concentrations of the gases remain the same. Under these conditions no segregation occurs. The gas mixture has a higher density than hydrogen, but a lower density than air. The lowest concentration is therefore measured on the ground. The lowest concentration of CO_2 is also measured on the ground, although CO_2 has a higher density than air. Under these conditions, the gas cloud stays together as a whole, where it is only diluted and does not separate.

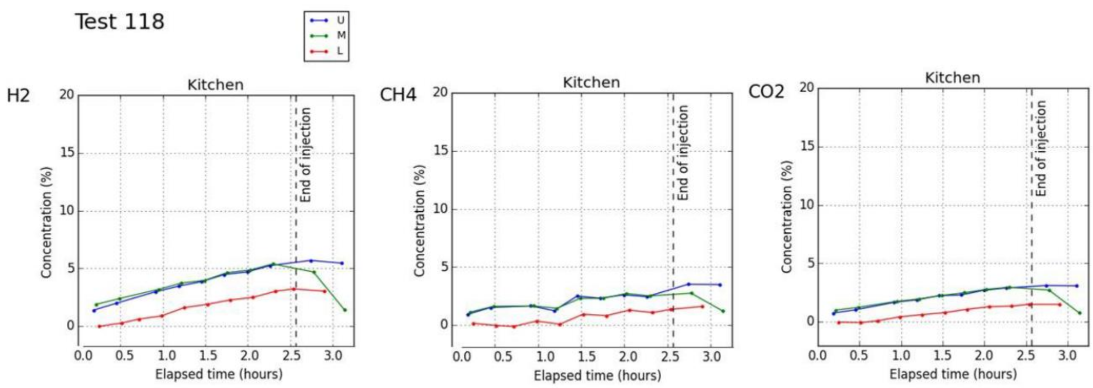

Figure 6: Concentration measured over time of the three components in town gas at three heights in the kitchen of the test house (U is upper(high), M is middle, L is low)

3.1.2 Modelling of a hydrogen leak, segregation and convection

The findings from the HyHouse study are confirmed with Computational Flow Dynamics (CFD) calculations by the Health and Safety Laboratory (HSE) [9]. CFD also calculates a layered build-up of the natural gas concentration, after a gas leak escapes into a room. This effect is also known as stratification.

Research and calculations by Pulles from 2020, show that stratification of the gas for a hydrogen leak corresponds to that of a methane leak. The concentration of hydrogen gas was higher because the volume of hydrogen from the simulated gas leak (a channel of 2.5 mm^2 and 3 mm in length) is three times as high (see figures 7 and 8).

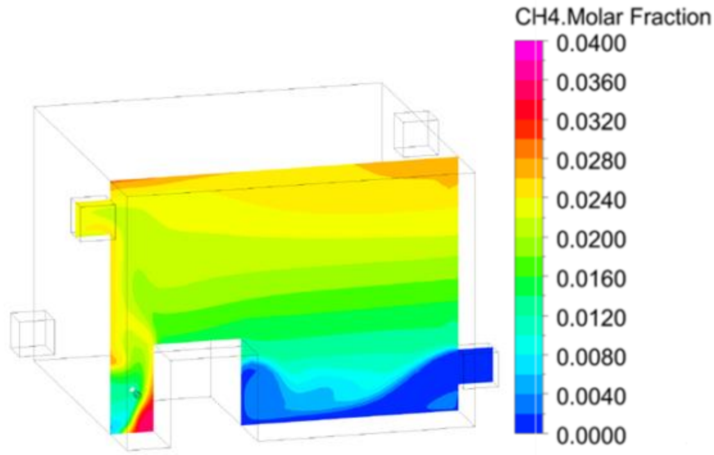

Figure 7: build-up of the methane content in a room (bottom right the gas leak, top left the exhaust of the ventilation)

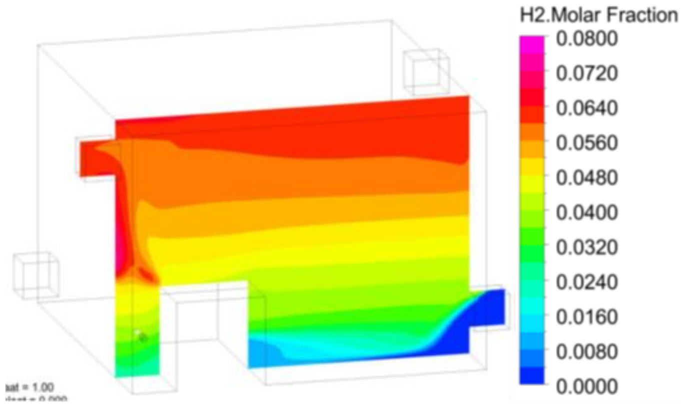

Figure 8: build-up of the hydrogen content in a room (bottom right the gas leak, top left the exhaust of the ventilation)

The spontaneous separation of a gas by laminar diffusion is very slow. Pulles has indicated this in a publication [7]. Based on the density difference of hydrogen and air, in a room with a stationary hydrogen/air mixture of 4000 ppm hydrogen (this is about 10% LEL), the concentration difference between the gas just below the 3 meter ceiling and the floor will be only 2 ppm. This effect is therefore negligible.

In the publication of Pulles [7] it is further explained that the stratification of a gas will not be removed by means of laminar diffusion. The laminar diffusion coefficient of hydrogen in air is about 0.7 10^{-4} m 2 /s. Over a height of 3 m, this means that a characteristic time of about 35 hours is needed to cancel the concentration differences in space. Methane has a diffusion coefficient about 3 times smaller in air than hydrogen and the characteristic time for levelling is therefore three times longer. In practice, the effect of convection will predominate over laminar diffusion. A typical air speed in a room is of the order of 0.1 m/s, from which follows a characteristic time of about half a minute. The laminar diffusion coefficient is therefore also of minor importance for hydrogen in air.

3.2 The behaviour of an odorant in hydrogen

The question remains whether odorant and hydrogen will separate spontaneously. The effect of separation by laminar diffusion is small for hydrogen, as mentioned above. The effect of convection is dominant, so it can be expected that the odorant will move with the gas cloud in a ventilated room.

As part of the H100 project, the School of Geosciences, University of Edinburgh, Kiwa Gastec, and SGN have investigated the odour of odorized hydrogen gas leaking into an interior space [1]. The aim is to determine whether a hydrogen leak can be detected as quickly as a natural gas leak.

The experiments were carried out in a space of 3m by 3m by 6m. These dimensions have been chosen so they are representative of the size of a living room. The gas is injected just above the floor surface. There are 9 measuring points scattered throughout the room. There are always three measuring points at a height of 0.3 metres, 1.5 metres, and 2.7 metres. A panel of 18 people smells the odour point at the measuring points at regular intervals. The panel members are outside the room and smell a so-called "sniffer". Methane and hydrogen sensors are also installed at the measuring points to measure the concentration of the gas. For an image of the experimental setup, see Figure 9.

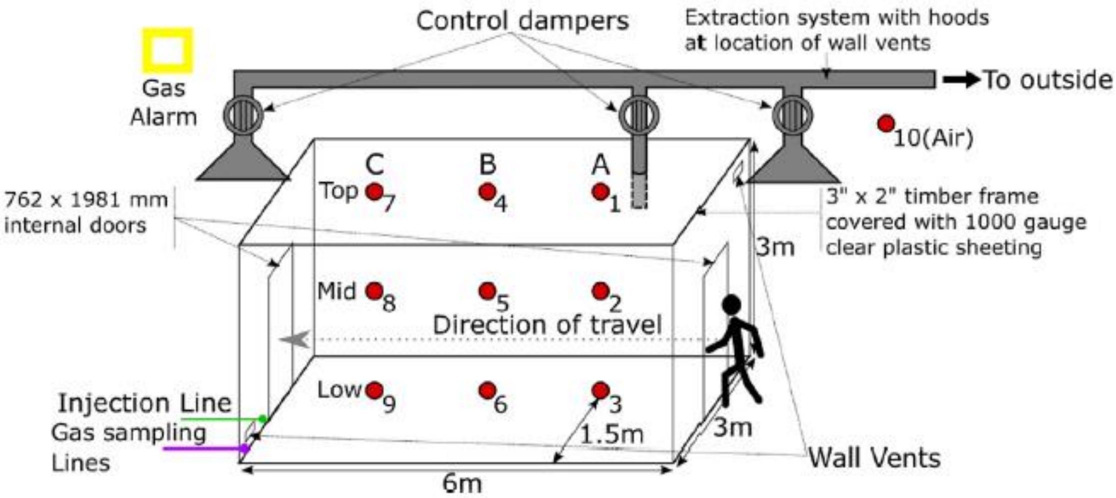

Figure 9: Experimental setup odorant detection in a confined space [1]

The following gas mixtures have been used for the experiments:
- hydrogen with odorant NB (78% tertiary butyl thiol and 23% dimethyl sulphide);
- hydrogen with diluted odorant (34% NB and 64% hexane);
- hydrogen with THT;
- natural gas with odorant NB.

The gas concentrations in the room built up slowly, with the following concentrations being reached after two hours:

- 10,000 ppm equivalent to 1% gas in air and 20% LEL (Lower Explosion Limit);
- 1,000 ppm equivalent to 0.1% gas in air;
- 500 ppm equivalent to 0.05% gas in air and 20 times below 20% LEL.

The criterion for a good odorant is that it must be smellable at 20% LEL.

Figures 10a and b show the results for odorized natural gas with a maximum concentration of 10,000 ppm.

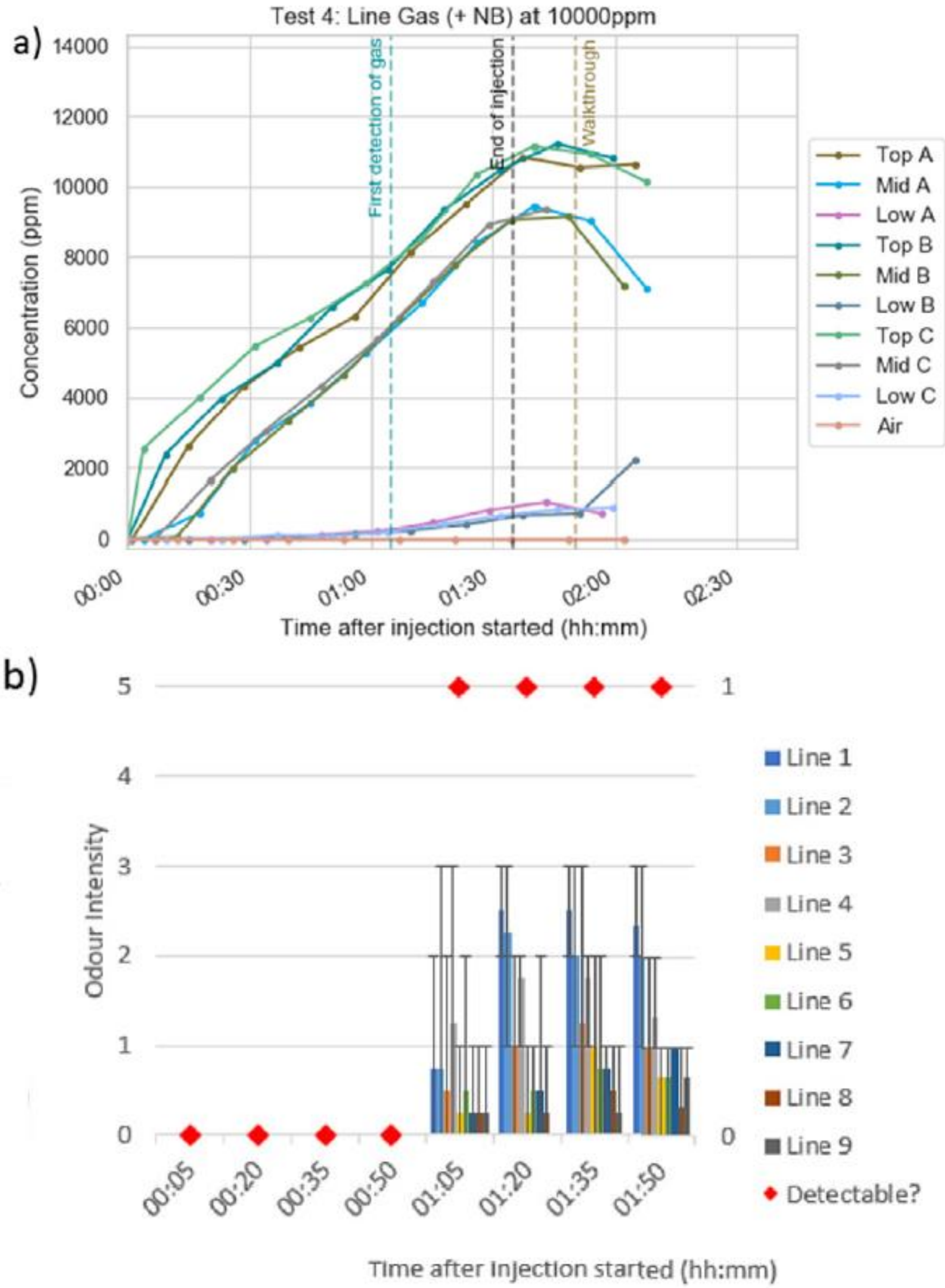

Figure 10 a and b: odorized natural gas added to a level of 10,000 ppm; the indication of the gas concentration measurement (A to C) and of the points at which an odour panel has been smelled (1 to 9) can be derived from figure 9

What is striking is that in this experiment, analogous to the HyHouse experiment, there is also a layered concentration. The concentration is highest at the top of the room and the lowest concentration is 30 cm above the floor surface. The gas is detectable at each sampling point but is strongest at the highest sampling points.

The criteria for smell are as follows:

1. very weak and possibly recognizable as a gas leak
2. weak but recognizable as a gas leak
3. easily detectable, clearly recognizable as a gas leak
4. strong smell
5. very strong smell

Figure 11a and b show the corresponding graphs for hydrogen odorized with NB.

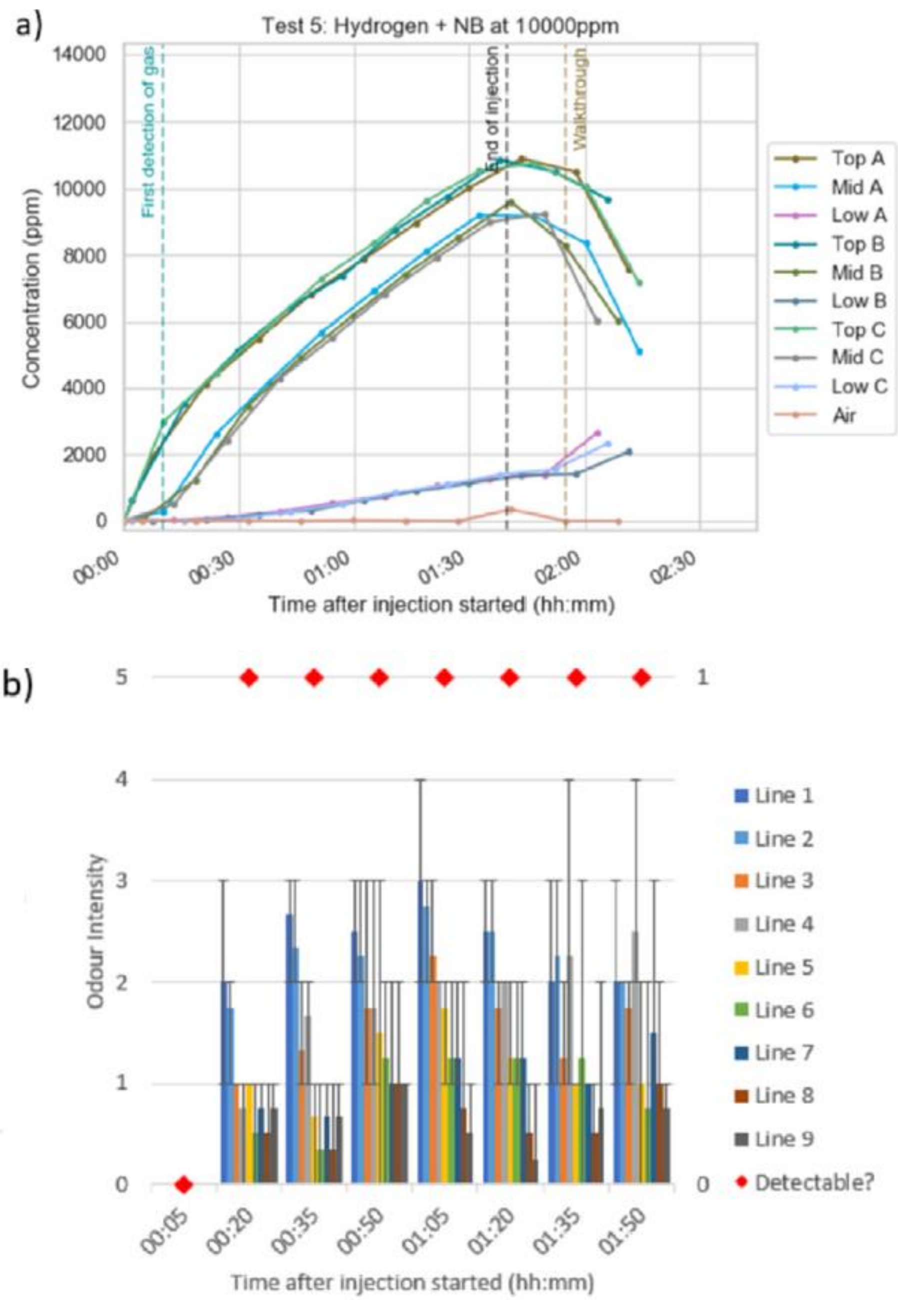

Figure 11: odorized hydrogen added to 10,000 ppm

After the set concentration in the model home has been reached, no more gas is added and the test panel members walk through the room and then indicate the odour experience at four places in the room, namely in the doorway and at measuring points 2, 5 and 8 (see figure 7).
Measuring point 8 is located just above the injection point. For the experiments in which the concentration in the model home is built up to 10,000 ppm of odorized gas, a slightly higher odour strength is measured on average than with the odour tests with sample points, in which the panel members are located outside the model home. When passing through the room, an average odour strength of 4 is observed in the room, which stands for a strong odour. This applies to both odorized natural gas and odorized hydrogen.

The researchers conclude that odorization of hydrogen is just as effective as odorization of natural gas. Small gas leaks are observed in a similar way. This conclusion is based on two methods, namely smelling at sample points where more and more gas is leaking into the home, and when walking through the home when 1% gas is present in the home.
It is further concluded that the odorant remains in the gas cloud under these conditions and that no separation of the odorant and the gas takes place. The latter applies to both natural gas and hydrogen.
Since the convection in a ventilated space has a much greater effect than the laminar diffusion (see section 4.2.1), this result is not surprising, but has now been substantiated by means of a test that simulates practice well.

3.3 Conclusions

Studies carried out in the context of the Hyhouse and H100 projects, as well as research by the British HSE and Pulles from the knowledge centre for gas network management (Kenniscentrum Gasnetbeheer) show that the distribution in air of a gas mixture and of the individual components in the gas mixture is determined by the density of the entire gas mixture. There will be no spontaneous separation of lighter or heavier components. There can be large differences between the gaseous components in terms of the laminar diffusion coefficients in air, but convection determines the diffusion in air and laminar diffusion is so slow that it does not play a role.

Experiments in the context of the Hy100 project have shown that this also applies to a mixture of an odorant in hydrogen. In the event of a gas leak, the odorant remains in the hydrogen cloud and no spontaneous separation occurs.

4. The behaviour of an odorant in hydrogen in soil

Here the results of the measurements on a mixture of THT in natural gas and in hydrogen are reported. This gas is passed through a sandy soil to simulate the effect of a gas leak. At the surface, the gas composition is measured with a micro gas chromatograph. It is already known from previous tests that methane moves faster upward through a sand column than THT [3].
These experiments will be carried out within the framework of the knowledge centre for gas network management (Kenniscentrum Gasnetbeheer) and these results will be shared with the HyDelta research program with the consent of the principal Netbeheer Nederland.
The results are not yet known and will be included in this report later, mid-2022. This report is therefore not yet a final version, but a provisional version.

5. Conclusions

The stability tests show that the three mixtures of 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.

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 behaviour is also supported by theoretical considerations. The difference between natural gas and hydrogen in air distribution is negligible.

In the case of a gas leak from a mixture of an odorant in hydrogen, 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, odorization of hydrogen is just as effective as odorization of natural gas.

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