ACCIDENTAL HYDROGEN RELEASE IN GC-LABORATORY; A CASE STUDY

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ABSTRACT

A 50-litre standard hydrogen gas cylinder was temporarily placed and used in a laboratory. The hydrogen gas was used for a flame ionization detector (FID) in gas chromatography (GC) instrument. On January 20, 2015 the safety relief valve on the pressure regulator blew open and released of about 340 g of hydrogen into a laboratory. The gas cloud did not ignite so there was no injury or damage. A full investigation with a complete course of action and reconstruction is presented to verify the cause of leakage and estimate the gas concentration of the dispersion and gas cloud. Preliminary simulation of a likely explosion pressure is given in the paper. If the gas cloud had ignited, the explosion pressure would most likely cause significant structural damage.

1.0 INTRODUCTION

This paper deals with an accidental hydrogen leak from a gas cylinder regulator. The hydrogen cylinder with the regulator was connected to a gas chromatograph (GC) with a flame ionization detector (FID). This was a temporarily instalment due to a renovation of the main laboratory. The hydrogen gas cylinder was placed inside the laboratory, due to a lack of hydrogen on the central gas system. The leak was detected by a hydrogen detector, which activated the alarm system. To stop the leakage, the hydrogen gas cylinder was manually closed.

The aim of the investigation after the incident was to i) identify the course of event prior to the leakage, ii) the cause of the leakage, the size of the leakage and ii) the severity of the accident. Simple calculations for release rate as well as simulations of the dispersion is part of the investigation. A test of the leaking regulator is performed to identify if the regulator is faulty. In addition, we studied a scenario where the hydrogen release was ignited. We have performed both simple calculations and a CFD-simulation of the event to estimate the explosion pressure.

Simple calculations and laboratory tests have identify the severity of the accident. Estimation of the pressure build from a possible ignition, using both simple models and CFD-simulation with FLACS will help to uncover the damages the release could have caused. Reviewing the course of events, the equipment and results, several important issues where found.

2.0 BACKGROUND

Due to renovation, the gas chromatograph had to be temporarily moved into another laboratory. The GC was operated on a weekly basis and could not be put temporarily out of service. Since the new laboratory did not have hydrogen on the central gas system, the hydrogen cylinder had to be placed inside the laboratory. To identify and avoid potential hazards a risk assessment was performed before the gas chromatograph moved into temporarily laboratory. The bulletins below summarizes the actions required.

- Installation of a hydrogen detector with an alarm system
- The size of the hydrogen cylinder should be limed to maximum 10-litre
- To operate the installation proper instructions, training and gas safety course was required

Since there was no 10-litre hydrogen cylinder in stock, it was decided to first use a 50-litre hydrogen cylinder that was nearly empty. As soon as this cylinder was empty, a 10-litre hydrogen gas cylinder was intended to replace the 50-litre gas cylinder. However, that was not the case; new 50-litre gas cylinder was installed.

Figure 1 shows a photo of the temporarily instalment before the event. Figure 2 shows an illustration of temporarily instalment.

Figure 1 - Temporarily GC instalment with hydrogen detector (red ring)

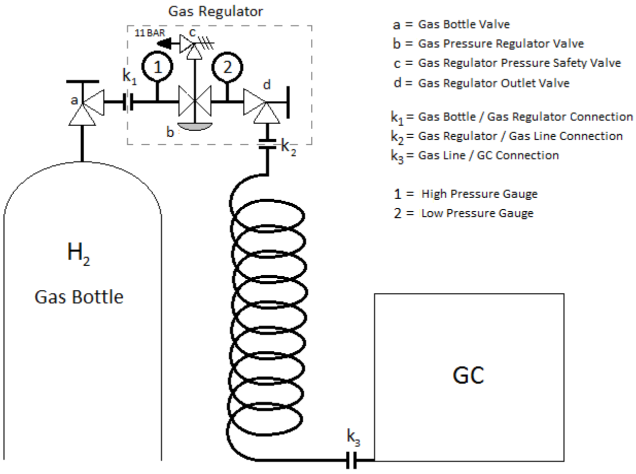

Figure 2 - Illustration of temporarily Instalment

2.1 Hydrogen Gas Detector

The red circle in the upper part of Figure 1 shows that the hydrogen gas detector was installed right above the hydrogen cylinder. The detector is connected to a Dräger QuadGuard controller located in the neighbouring laboratory. The Dräger QuadGuard controller unit has three detectors connected. One hydrogen and one carbon monoxide detector is located in the same room as the QuadGuard unit (the neighbouring laboratory) and the hydrogen detector shown in Figure 1 (The laboratory containing the FID-GC).

Dräger QuadGuard controller unit has two alarm levels for hydrogen leakages. A level one alarm will be activated when the hydrogen mixture has reached 10% of the lower explosion limit (LEL). The level two alarm will be activated when the hydrogen mixture reaches 25 % LEL. Each alarm can be identified by a distinctive sound. Sound horns and light signals are installed in both laboratories and in the corridor outside the laboratories. [1]

2.2 Hydrogen Pressure Regulator

A pressure regulator suited for hydrogen was used to regulate the flow from the hydrogen cylinder to the gas chromatograph. The regulator has maximum operation pressure of 230 barg on the high-pressure side and maximum operation pressure of 10 barg on the low-pressure side. The regulator is equipped with a pressure safety relief valve on the low-pressure side, which will open when the low pressure exceeds 11 barg. There is no pressure safety valve to reduce the pressure on the high-pressure side. Figure 3 shows a cross section of the gas regulator.

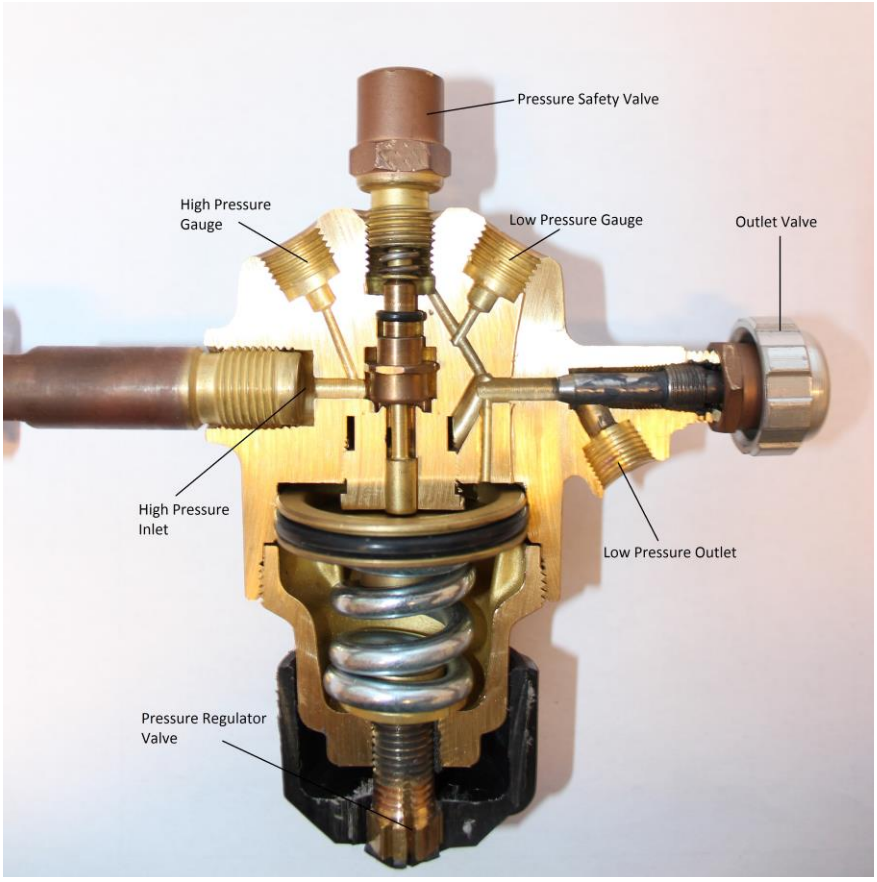

Figure 3 - Hydrogen gas regulator

The age of the hydrogen gas regulator was unknown until after the event, but was confirmed by a supplier to be almost 40 years. The hydrogen pressure regulator was produced 1975, week number 25. Along with the model number, the year and week the model was manufactured is located on the back of the regulator, in that order.

3.0 THE EVENT

On the 16th of January 2015, the first 50 litre hydrogen gas cylinder was depleted and was changed to continue operation. Due to a miscommunication between the risk assessment team and the instrument operator, a new 50-litre hydrogen gas cylinder was ordered and installed. The new installed 50-litre hydrogen cylinder showed 210 barg in the high-pressure gauge. A small irregularity in the behaviour of the hydrogen pressure regulator was noticed when adjusting to the set pressure. The pressure seemed to increase slowly relative to the adjustment done on the gas-pressure regulator valve (valve b in Figure 2). After reaching the desired pressure of 4 barg, a leak check was performed with Digitron

DGS-10. During the leak test, the gas-regulator outlet valve (valve d in Figure 2) was closed. No leaks were found. Before leaving for the weekend, the gas cylinder valve (valve a in Figure 2) was closed.

On the 20th of January, the instrument operator return to turn on the gas chromatograph saw that the pressure in the system had drop to 0 barg. Since the regulator outlet valve was closed (valve d in Figure 2), a leak was suspected. The regulator was detached and then reattached. After opening the gas cylinder valve (valve a in Figure 2), a leak check was performed. The high-pressure gauge showed 210 bars and no leaks where found. Before operating the gas chromatograph, the instrument operator noticed that the low-pressure gauge showed just over 10 barg. The instrument operator then decided to bleed down the pressure slowly (10 ml/min) from the low-pressure to and through the gas chromatograph. This was done by closing the gas pressure regulator valve (valve b in in Figure 2 and opening the regulator outlet valve. At this point, the gas cylinder valve and the gas regulator outlet valve was open, and the gas pressure regulator valve was closed. While the pressure was bleeding down, the instrument operator decided to go back to the office and retrieve some items before returning to the laboratory. Before leaving the laboratory, the instrument operator met and talked to the laboratory safety officer explaining the situation. While away, the hydrogen gas leak occurred.

The leak started between 1 and 3 minutes after the instrument operator had left the laboratory, the Dräger QuadGuard controller detected a gas leakage and sounded the alarm. Laboratory safety officer sitting across the corridor heard the alarm and went into the neighbouring laboratory where the Dräger QuadGuard control unit is to verify which detector that as raised the alarm and what type of leak it was. QuadGuard control unit showed that there was a hydrogen leakage in the laboratory containing the FID-GC. The laboratory safety officer then rushed to the laboratory where the leakage was and manually closed the gas cylinder valve (valve a in in Figure 2). After closing the gas cylinder valve, the laboratory safety officer exited the laboratory and waited until the alarm level was down to a level one before entering.

There was no human injuries nor damages to the laboratory. The gas cylinder was removed immediately. All hydrogen related operations where temporarily shut down until the cause of the leak was established and a new risk assessment was done.

4.0 RECONSTRUCTION AND STUDY

A reconstruction of the event showed that the leakage lasted approximately 30 seconds. Mounting a new hydrogen gas regulator on the hydrogen gas cylinder showed that the pressure had dropped from 210 barg to 110 barg. A steady state isothermal calculation using the NIST database for determining hydrogen properties showed that the total release between initial and final pressure was 340 grams of hydrogen. This will at atmospheric pressure result in a gas volume of 4 m^3. [2]

Using Abel-Noble equation of state and assuming adiabatic choked flow, the mass flow rate and total release hydrogen mass can be calculated. Figure 4 shows the change in the mass flow rate and Figure 5 shows the hydrogen released during the leakage. [3]

The total hydrogen release calculated by Abel-Nobel equation of state corresponds very well with steady state isothermal (using NIST database) calculation.

The floor area of the laboratory room was estimated to be 51 m^2. With a 30 % stoichiometric and a 15% hydrogen gas cloud, the height of the cloud was estimated to be 0.266 m and 0.533 m respectively. The volume of the laboratory was estimated to be 170 m^3 without considering the volume of cabinets, fume hoods, benches, ventilation pipes etc. The calculated pressure increase if ignited assuming a closed volume was 0.65 bars. According to *"V.J Clancey, Diagnostic Features of Explosion Damage"*, the damage would be between a loaded train boxcars completely demolished (0.62 barg) and probable total destruction of buildings (0.689 barg) [4].

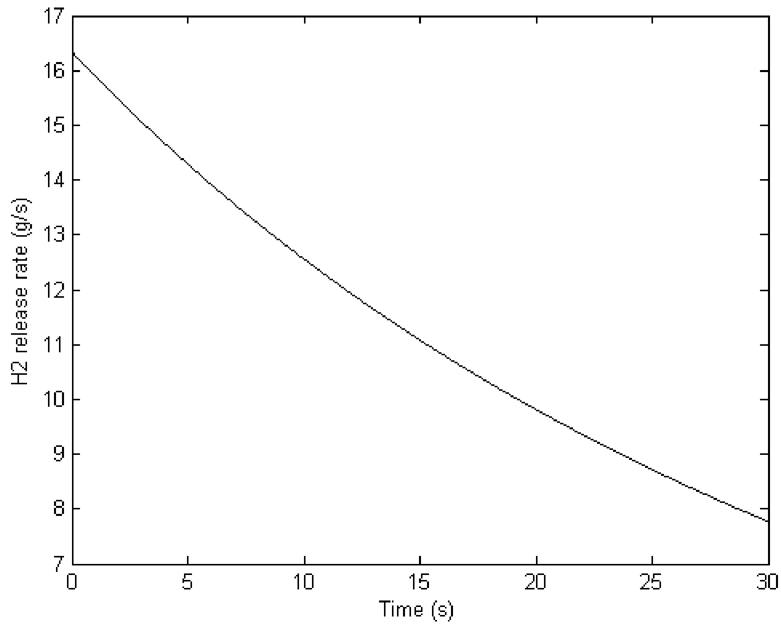

Figure 4 - Mass flow rate, initial 21 MPa, nozzle diameter 1.3 mm, Vol 50 dm^3

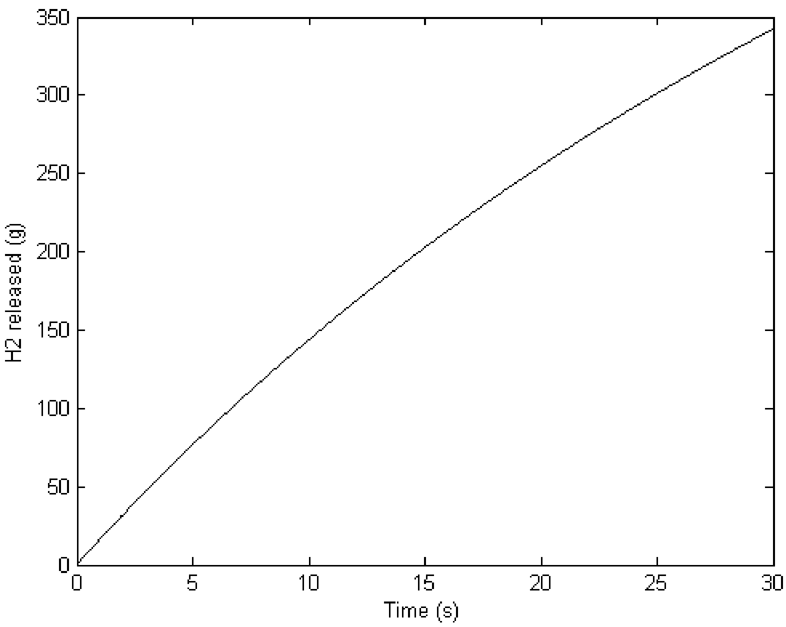

Figure 5 - Hydrogen released, initial 21 MPa, nozzle diameter 1.3 mm, Vol 50 dm^3

To recreate the incident a controlled test was performed with the same cylinder and the same leaking regulator. In this test the gas cylinder had about 100 bar pressure. The test setup is shown in Figure 6. Both the pressure regulator valve and the outlet regulator valve were closed while the cylinder valve was opened. The gas flowed out of the safety valve showing that the regulator was faulty. To visualize the jet height the released hydrogen was ignited. Figure *7* shows a Background Oriented Schlieren (BOS) image of the ignited jet. By averaging 200 frames from a high speed film the height of the flame was measured to approximately 1.5 m. This height is in accordance to the calculation method by

Saffers and Molkov [6] when using 1.3 mm nozzle diameter and 100 bar cylinder pressure. Using the same calculation method with cylinder pressure of 210 barg, as was the case in the incident, the jet height would be about 2 m. [5]

The test and calculation shows that a possible ignited jet would reach the ceiling in the laboratory and shows that the concentration in the core of the unreacted jet was initially close to stoichiometric at the ceiling height.

Figure 6 - Test setup

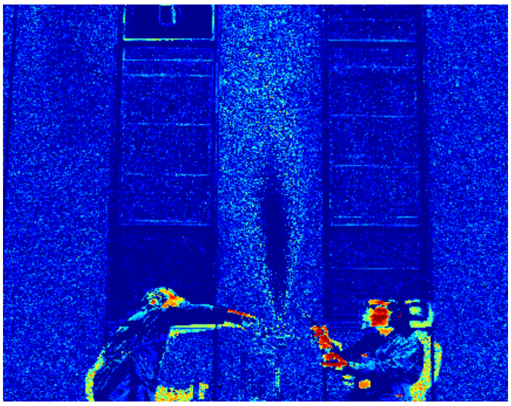

Figure 7 - Turbulent flame height

5.0 FLACS

We have performed a CFD-simulation of the event to estimate the explosion pressure in case of a homogeneous gas cloud and an open door in to the laboratory. Figure 8 shows the geometry of the laboratory generated in CASD-FLACS.

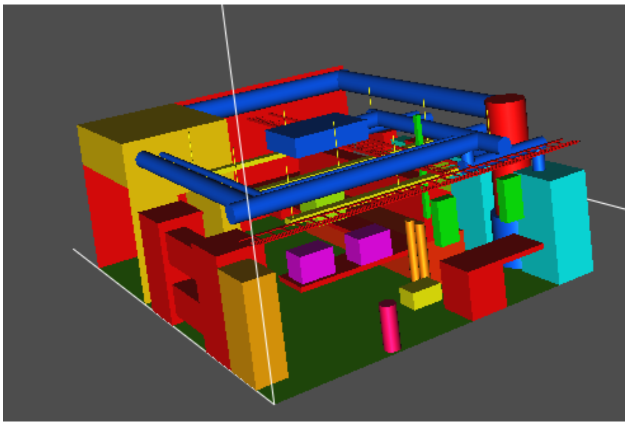

Figure 8 - Laboratory Geometry

Figure 9 shows the pressure in the room reached 0.4 barg in the FLACS simulation, which is in the same order as the simple calculation shown in the previous section.

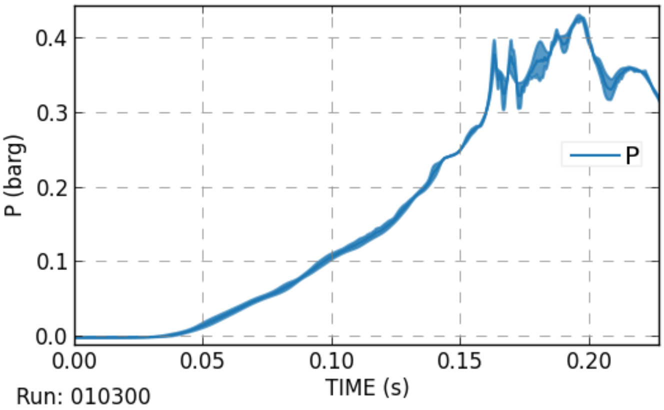

Figure 9 - Explosion pressure versus time

6.0 LESSONS LEARNED

The use of a nearly depleted 50-litre hydrogen cylinder was a breach of inherent safety and should never have happen. When the GC was installed, a new 10-litre hydrogen cylinder should have been ordered and installed before using the instrument.

Using a 10-litre hydrogen cylinder instead of a 50-litre would have reduced the released hydrogen by 55% even if the 10-litre hydrogen cylinder was completely depleted. Compared to a completely depleted 50-litre hydrogen cylinder, the reduction would be 80%.

Having a hydrogen alarm system may have saved the laboratory from a severe accidental explosion. There were no personnel inside the laboratory during the leak so without the alarm system the whole hydrogen gas cylinder would probably be released into the room. This would create a gas cloud with a height of about 1.2 meters with 15 % stoichiometric hydrogen (without considering other volumes in the room). This gas cloud would significantly increase the probability for ignition.

The age of the hydrogen gas regulator used was difficult to determine by reading the numbers printing on the back. The age was first established after contacting a supplier. Had the age of the gas regulator been know during the installation it would most likely not been used.

A lack of service on the gas regulators has also been identified. A service for the gas regulators in use as been established as a result of this event.

The pressure safety valve on the gas regulator does not work as a safety feature when the safety valve releases the gas into an environment that contains several ignition sources. To work as a safety feature the gas needs to be routed to a safe ventilation point. A similar event happened at a commercial facility in 05/03/2013, where a failure of the pressure safety valve occurred. One of the conclusions from the investigation was that if the safety valve shall function as a safety feature the gas needs to be released in a safe location. [7]

The evacuation from the all laboratories where followed when the alarm initiated. The evacuation from the office across the corridor was not equally successful. The office personnel exited their offices, but remained in the corridor and not exiting the building. The problem was a combination of curiosity and poor evacuation routines for the offices.

Temporarily installation should be treated with regards to safety and risk, as permanent installed equipment. All precautions and risk preventions performed must be communicated to users, especially to the responsible personnel, so that the risk of miscommunication is reduced to a minimum.

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